[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

Geometrical Isomerism and Absorption Spectra of Dinitrophenylhydrazones

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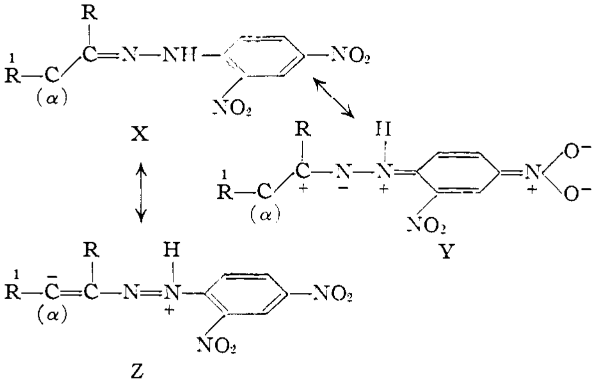
The infrared and ultraviolet absorption spectra of forty-three 2,4-dinitrophenylhydrazones (DNP's), including several pairs of geometrical isomers about the C=N bond, have been examined. A method for the assignment of configuration (*syn-* or *anti-*) to most of the DNP's studied has been developed. This method is based on two general observations: (1) In one isomer of a pair of α-methoxy DNP's (for example the pair of α-methoxypropiophenone DNP's IVcA and IVcB) the band corresponding to the N-H stretching vibration appeared (broader and stronger) shifted by about 0.1 μ in the direction of longer wave lengths, relative to the unsubstituted DNP (*i.e.*, propiophenone DNP IVa, in the example used). Hence, in that isomer, the N-H and CH_3O groups interact and must therefore be on the same side of the C=N bond. (2) The ultraviolet absorption maximum of *syn*-α-methoxypropiophenone DNP (IVcA) (NH- and CH_3O on the same side of the C=N bond) appeared displaced by +5 mμ, relative to propiophenone DNP (IVa) while the maximum of *anti*-α-methoxypropiophenone DNP (IVcB) (NH- and CH_3O on opposite sides of the C=N bond) appeared displaced by −16 mμ, relative to IVa. On the assumption that the hypsochromic shift is due to a change in configuration about the C=N bond, the propiophenone DNP at hand is considered to be the *syn*-isomer (IVaA). The effect of α-substituents (Cl, Br, CH_3O, AcO, α,β-unsaturation) and of ring size and shape, *within a given stereochemical series*, on the ultraviolet absorption spectrum of DNP's has been assessed and interpreted in terms of stabilization of excited and ground states and of steric inhibition of resonance.

I. Introduction

The strong band (log ϵ 4.4) exhibited by 2,4-dinitrophenylhydrazones (X) (DNP's) in the ultraviolet between 350 and 390 mμ has been attributed to electronic transitions involving excited states to which forms -Y are supposed to make an appreciable contribution.[2] It was pointed out[2b,c,d] that variations in the structure of the parent carbonyl compound from which the DNP is derived are apt to have relatively small effects on the position and intensity of the absorption maxima of DNP's. The significant bathochromic–hyperchromic effect observed in going from R = alkyl to R = aryl in X has, however, been appreciated. The contribution of resonance forms such as Z, has also been discussed.[2]



Although clearly relevant to the interpretation of ultraviolet absorption spectra, the question of the stereoisomerism of DNP's about the C=N bond has received little attention. This is in contrast to other cases of N=N and C=N stereoisomerism as in the azo-compounds,[3] the oximes,[4] the diazocyanates[5] and the triazenes[6] in which light absorption and configuration have been the subject of extensive correlations. In a few instances isomeric pairs of phenyl and 2,4-dinitrophenylhydrazones have been reported[7] and in a recent case, that of the 2-acylpyridine phenylhydrazones studied by Kuhn and Munzing,[8] configurations were assigned to the isomers on the basis of the formation of an 8-aza-indazolium salt.

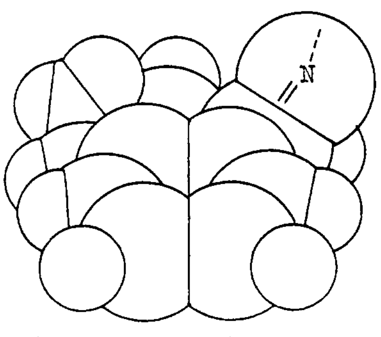


Fig. 1.—*syn*-Benzosuberone DNP.

During a study of the action of carbonyl reagents on α-substituted ketones[9] we prepared a number of DNP's, some of which could be isolated in two isomeric forms appearing to differ in configuration about the C=N bond. Since the occurrence of polymorphism and isomorphism among DNP's[10] introduces elements of uncertainty in comparisons involving this type of carbonyl derivative, it was

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[1] From the Ph.D. thesis of A. F. Kirby. Presented at the Meeting-in-Miniature of the New York Section of the American Chemical Society, Brooklyn, New York, February 20, 1953.

[2] (a) F. Bohlmann. *Chem. Ber.*, **84**, 490 (1951); (b) C. Djerassi and E. Ryan, THIS JOURNAL, **71**, 1000 (1949); (c) H. H. Szmant and J. J. Planinsek, *ibid.*, **72**, 4042 (1950); (d) J. D. Roberts and C. Green, *ibid.*, **68**, 214 (1946); (e) E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 498 (1945); (f) R. Huisgen and W. Rapp, *Chem. Ber.*, **85**, 826 (1952); (g) R. Heilmann, G. DeGaudemores and P. Arnaud, *Compt. rend.*, **234**, 1177 (1952); (h) T. Canback, *Farmacevtisk Revy*, **48**, 217 (1949); (i) Ramart-Lucas, J. Hoch and M. Martynoff, *Bull. soc. chim.*, [5] **4**, 481 (1937).

[3] (a) A. H. Cook, D. G. Jones and J. B. Polya, *J. Chem. Soc.*, 1315 (1939); (b) W. R. Brode, J. H. Gould and G. M. Wyman, THIS JOURNAL **74**, 4641 (1952); (c) W. R. Brode, J. H. Gould and G. M. Wyman, *ibid.*, **75**, 1856 (1953).

[4] R. F. Raffauf, *ibid.*, **68**, 1765 (1946).

[5] R. J. Le Fevre and I. R. Wilson, *J. Chem. Soc.*, 1106 (1949).

[6] R. J. Le Fevre and T. H. Liddecoet, *ibid.*, 2743 (1951).

[7] (a) For a recent review see G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 346; (b) H. Bredereck, *Ber.*, **65B**, 1833 (1932); (c) H. Bredereck and E. Fritzsche, *ibid.*, **70**, 802 (1937).

[8] R. Kuhn and W. Munzing, *Chem. Ber.*, **85**, 29 (1952).

[9] Part I, F. Ramirez and A. F. Kirby, THIS JOURNAL, **74**, 4331 (1952); Part II, F. Ramirez and A. F. Kirby, *ibid.*, **75**, 6026 (1953).

[10] *Cf.* (a) W. Dirscherl and H. Nahm, *Ber.*, **73B**, 448 (1940); (b) G. Matthiessen, *Arch. Pharm.*, **284**, 62 (1951); (c) W. M. D. Bryant, THIS JOURNAL, **60**, 2814 (1938); (d) C. F. H. Allen and J. H. Richmond, *J. Org. Chem.*, **2**, 222 (1937).

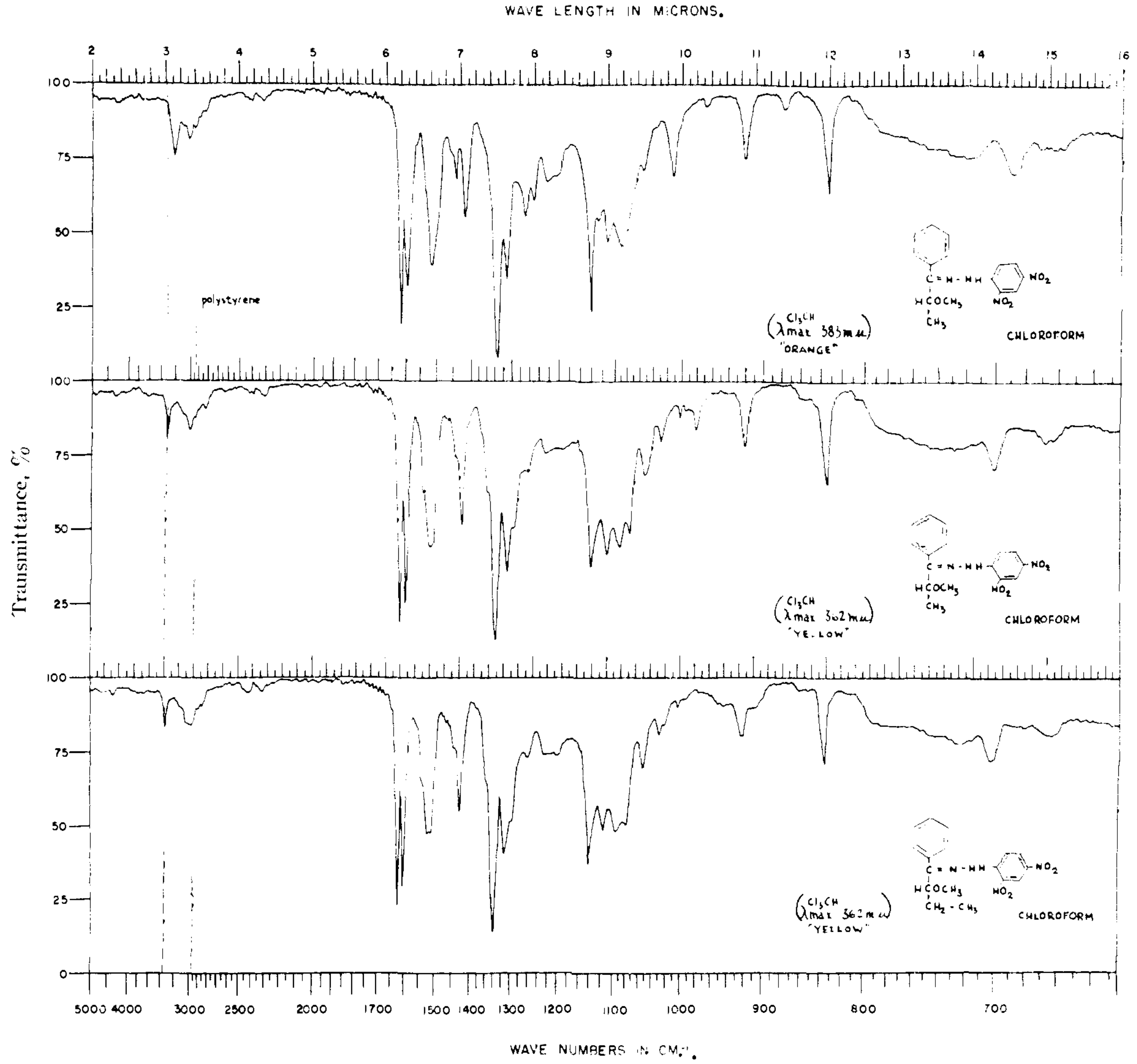

Fig. 2.

deemed necessary in our work[9] to rely partly on ultraviolet and infrared absorption data.[11] It is the purpose of the present communication to show how these spectroscopic data can be used to assign configurations to a relatively large number of DNP's. Likewise, it will be shown that a knowledge of the configurations of the DNP's permits a number of correlations between structure and geometrical isomerism of DNP's on the one hand and ultraviolet absorption spectrum on the other hand.

II. Experimental

The preparation and physical constants of the compounds discussed in this paper are described in parts I and II.[9] These contain also the values of the ultraviolet absorption maxima and their extinction coefficients ϵ, determined in chloroform solution, on the analytical samples, in a Cary Recording Spectrophotometer Model 11, with chloroform as reference standard. The spectra of some of the compounds had already been determined and these will be found in ref. 2. For purpose of comparison they were redetermined under identical instrumental and experimental conditions.

In part I[9] values of log ϵ were given; the actual ϵ values are included here for convenience in comparisons (see Chart I for formulas). $\epsilon \times 10^{-4}$ of DNP's at the respective λ_{max}: cyclohexanone (Ia), 2.34; 2-bromocyclohexanone (Ib), 2.45; 2-chlorocyclohexanone, 2.37; 2-methoxycyclohexanone (Ic), 2.44; 2-cyclohexen-1-one (Ie), 2.70; 2,2-dimethylcyclohexanone (IIa), 2.27; 6,6-dimethyl-2-bromocyclohexanone (IIb), 2.34; 6,6-dimethyl-2-methoxycyclohexanone (IIc), 2.50; 6,6-dimethyl-2-cyclohexen-1-one (IIe), 2.68; 1-keto-1,2,3,4-tetrahydrophenanthrene (XIIIa), 3.30; 2-bromo-1-keto-1,2,3,4-tetrahydrophenanthrene (XIIIb), 3.30.

Infrared spectra were determined in approximately 3% chloroform solutions in a Baird Associates, Inc., spectrophotometer (sodium chloride prism, 0.1-mm. cell thickness). The curves shown are tracings of the actual recordings, the curves being aligned at 3.40 μ (2940 cm.$^{-1}$).

III. Results and Discussion

Geometrical Isomerism of 2,4-Dinitrophenylhydrazones.—Chart I illustrates the four general types of 2,4-dinitrophenylhydrazones (DNP's) included in this study: (i) derivatives of cyclohexanone (I) and of 2,2-dimethylcyclohexanone (II); (ii) derivatives of phenylalkyl ketones including

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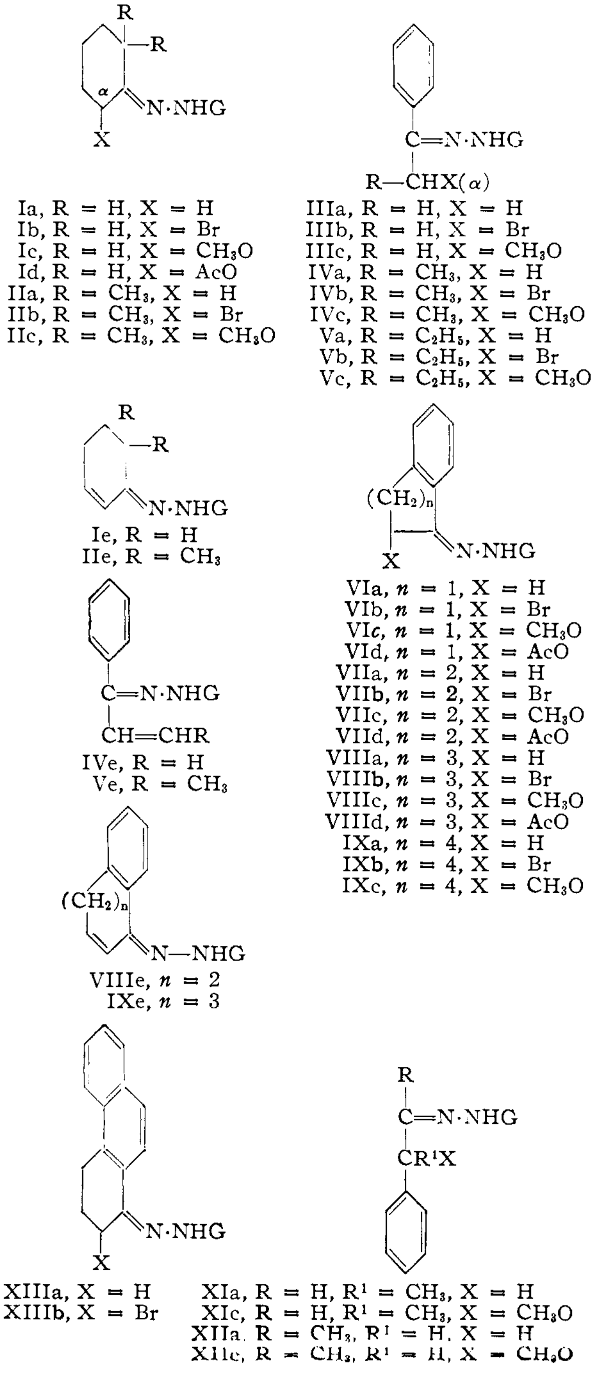
[11] Other elements of uncertainty arising from possibility of cyclizations to heterocyclic systems are discussed in ref. 9.

acetophenone (III), propiophenone (IV) and butyrophenone (V); (iii) derivatives of indanone (VI), tetralone (VII), benzosuberone (VIII), 2,3-benzocycloöctene(2)-one(1) (IX) and 1-keto-1,2,3,4-tetrahydrophenanthrene (XIII); (iv) derivatives of α-phenylpropionaldehyde (XI) and of α-phenylacetone (XII) in which the aromatic ring is not conjugated to the hydrazone group. With the exceptions noted in the Chart, five kinds of derivatives of each structural type were considered: (a) the unsubstituted DNP's; (b) the α-bromo DNP's; (c) the α-methoxy DNP's; (d) the α-acetoxy DNP's and (e) the α,β-unsaturated DNP's. In several instances two isomeric forms of a particular DNP could be isolated; these will be distinguished by means of the notations A and B.

CHART I

$G = 2,4\text{-}(NO_2)_2\cdot C_6H_3$



Ia, $R = H, X = H$
Ib, $R = H, X = Br$
Ic, $R = H, X = CH_3O$
Id, $R = H, X = AcO$
IIa, $R = CH_3, X = H$
IIb, $R = CH_3, X = Br$
IIc, $R = CH_3, X = CH_3O$

IIIa, $R = H, X = H$
IIIb, $R = H, X = Br$
IIIc, $R = H, X = CH_3O$
IVa, $R = CH_3, X = H$
IVb, $R = CH_3, X = Br$
IVc, $R = CH_3, X = CH_3O$
Va, $R = C_2H_5, X = H$
Vb, $R = C_2H_5, X = Br$
Vc, $R = C_2H_5, X = CH_3O$

Ie, $R = H$
IIe, $R = CH_3$

VIa, $n = 1, X = H$
VIb, $n = 1, X = Br$
VIc, $n = 1, X = CH_3O$
VId, $n = 1, X = AcO$
VIIa, $n = 2, X = H$
VIIb, $n = 2, X = Br$
VIIc, $n = 2, X = CH_3O$
VIId, $n = 2, X = AcO$
VIIIa, $n = 3, X = H$
VIIIb, $n = 3, X = Br$
VIIIc, $n = 3, X = CH_3O$
VIIId, $n = 3, X = AcO$
IXa, $n = 4, X = H$
IXb, $n = 4, X = Br$
IXc, $n = 4, X = CH_3O$

IVe, $R = H$
Ve, $R = CH_3$

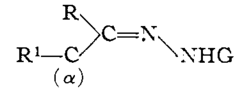
VIIIe, $n = 2$
IXe, $n = 3$

XIIIa, $X = H$
XIIIb, $X = Br$

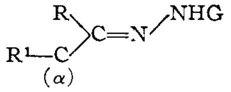
XIa, $R = H, R^1 = CH_3, X = H$
XIc, $R = H, R^1 = CH_3, X = CH_3O$
XIIa, $R = CH_3, R^1 = H, X = H$
XIIc, $R = CH_3, R^1 = H, X = CH_3O$

Examination of the absorption spectra of the DNP's (in chloroform solutions) in the infrared and the ultraviolet suggested a method for the assignment of configuration to these compounds about the C═N bond. This method is based on the following observations.

(1) Consider the *infrared absorption spectra* of the two isomeric forms of α-methoxypropiophenone DNP (IVcA and IVcB). In one of these spectra, that of the methoxy DNP IVcB, the band corresponding to the N–H stretching vibration was found at the same wave length (3.00 μ) as that of the corresponding vibration in the unsubstituted DNP, *i.e.*, propiophenone DNP (IVa). In the spectrum of the isomeric methoxy DNP IVcA, however, the N–H band was found (broader and stronger) shifted by about 0.1 μ in the direction of longer wave lengths (see curves). The same relationship was observed in the infrared spectra of the isomeric α-methoxybutyrophenone DNP's (VcA and VcB), relative to the spectrum of butyrophenone DNP (Va). On the assumption that the observed displacements of the N–H band in the methoxy DNP's are due to interaction between the N–H and the CH_3O groups (hydrogen bonding), the isomers designated as A-isomers were considered to have the *syn*-configuration, defined as that in which the NHG group and the α-carbon are on the same side of the C═N bond.



Series-A (*syn*-isomer)



Series-B (*anti*-isomer)

The only isolable isomeric forms of 2-methoxycyclohexanone DNP (Ic) and 6,6-dimethyl-2-methoxycyclohexanone DNP (IIc) were assigned to the A-series (*syn*) since in their spectra, the shift of the N–H band was observed. The α-methoxy-α-phenylpropionaldehyde DNP (XIc) at hand, whose spectrum showed the N–H band at the same wave length as that of the parent DNP, *i.e.*, α-phenylpropionaldehyde DNP (XIa), was assigned to the B-series (*anti*).

(2) Consider now the *ultraviolet absorption spectra* of the two isomeric forms of α-methoxypropiophenone DNP (IVcA and IVcB), and compare these spectra with that of the only isolable form of the parent DNP, *i.e.*, propiophenone DNP (IVa). It was observed that in going from the parent DNP (IVa) to the *syn*-methoxy DNP (IVcA) a small ($\Delta\lambda = +5$ mμ) but significant bathochromic shift of the absorption maximum resulted. On the other hand, the change involving the same parent DNP (IVa) and the *anti*-methoxy DNP (IVcB) resulted in a relatively large ($\Delta\lambda = -16$ mμ) ***hypsochromic*** shift. This hypsochromic shift must be the result of a change in configuration about the C═N bond. Clearly then, our propiophenone DNP (IVa) and *anti*-α-methoxypropiophenone DNP (IVcB) belong to opposite geometrical series. The generality of this type of argument

is brought out by similar comparisons involving *syn*- and *anti*-α-methoxybutyrophenone DNP's (VcA and VcB) and the only isolable form of butyrophenone DNP(Va).

It is of interest to note at this point that the magnitude of the effect exerted in the ultraviolet absorption by a methoxyl group situated in the α-position of a DNP is small ($\Delta\lambda$ = *ca.* 5 mμ), and that the direction of the effect is a function of spatial factors. Thus, *syn*-2-methoxycyclohexanone DNP (IcA) absorbs at a higher wave length than cyclohexanone DNP (Ia) ($\Delta\lambda = +7$ mμ); on the other hand, *anti*-α-methoxy-α-phenylpropionaldehyde (XIcB) absorbs at a shorter wave length than α-phenylpropionaldehyde DNP(XIa) ($\Delta\lambda = -4$ mμ). Similar observations can be made on the pairs: *syn*-6,6-dimethyl-2-methoxycyclohexanone DNP (IIcA) and 2,2-dimethylcyclohexanone (IIa); *anti*-α-methoxy-α-phenylacetone (XIIcB) and α-phenylacetone (XIIa); *anti*-2-methoxybenzosuberone DNP (VIIIcB) and *anti*-benzosuberone DNP (VIIIaB).

TABLE I

ULTRAVIOLET ABSORPTION MAXIMA OF UNSUBSTITUTED 2,4-DINITROPHENYLHYDRAZONES (DNP's) RELATIVE TO CYCLOHEXANONE DNP (Ia)

$\lambda^{Ia}{}_{max}$ 366 mμ; ϵ^{Ia} 2.34×10^4; $\Delta\lambda = \lambda_{max} - \lambda^{Ia}{}_{max}$; $\%\Delta\epsilon = [(\epsilon - \epsilon^{Ia})/\epsilon^{Ia}]\ 100$.

Compound	Δλ, mμ (% Δε)
1-Keto-1,2,3,4-tetrahydrophenanthrene (XIIIa)	+25 (+41)
syn-Indanone (VIaA)	+20 (+28)
syn-Tetralone (VIIaA)	+19 (+22)
syn-Benzosuberone (VIIIaA)[a]	+ 6 (+ 9)
anti-Benzosuberone (VIIIaB)[a]	+ 3 (0)
2,3-Benzocyclooöctene(2)-one(1) (IXa)[b]	0 (+ 6)
syn-Acetophenone (IIIaA)	+12 (+12)
syn-Propiophenone (IVaA)	+12 (+12)
syn-Butyrophenone (VaA)	+14 (+12)
2,2-Dimethylcyclohexanone (IIa)[b]	+1 (+ 3)
α-Phenylacetone (XIIa)[b]	− 4 (− 2)
α-Phenylpropionaldehyde (XIa)[b]	− 9 (−1)

[a] The isomer which absorbs with greater intensity at a longer wave length is taken as the *syn*-isomer. (The NHG and conjugated aromatic ring are then on opposite sides of the C═N bond.) VIIIaB but not VIIIaA has a second maximum at 258 mμ. [b] Not enough information for a definite assignment of configuration; see, however, footnote 12.

TABLE II

SHIFTS IN THE ULTRAVIOLET ABSORPTION MAXIMA OF 2,4-DINITROPHENYLHYDRAZONES (DNP's) UPON SUBSTITUTION AT THE α-CARBON

The values given under each column represent the shifts in λ_{max} and in ε observed upon replacement of an α-hydrogen in the parent DNP given at the top of the column by the substituent indicated in the first column. $\Delta\lambda = \lambda^{subst}_{max} - \lambda^{unsubst}_{max}$; $\%\ \Delta\epsilon = [(\epsilon^{subst} - \epsilon^{unsubst})/\epsilon^{unsubst}]\ 100$

Subst. X on α-carbon	Cyclohexanone (I) Δλ, mμ (% Δε)	2,2-Dimethylcyclohexanone (II)[a] Δλ, mμ (% Δε)	α-Phenylpropionaldehyde (XI)[a] Δλ, mμ (% Δε)	α-Phenylacetone (XII)[a] Δλ, mμ (% Δε)
Br (b)	−6 (+5)[b]	−3 (+3)	....	....
Cl	−9 (0)	....	....	....
CH_3O (c)	A + 7 (+4)[c]	A + 6 (+10)	B − 4 (0)	B − 3 (+1)
AcO (d)	−8 (−4)	....	....	....
α,β-unsat. (e)	+12 (+15)	+11 (+20)	....	....

[a] As explained in footnote 12, the configuration of this unsubstituted DNP is not regarded as unequivocally established. [b] Example: the replacement of an α-hydrogen in cyclohexanone DNP (Ia) by a bromine atom to yield 2-bromocyclohexanone DNP (Ib) of unknown configuration, results in a hypsochromic shift, $\Delta\lambda = -6$ mμ and a hyperchromic shift $\%\ \Delta\epsilon = +5$. [c] Example: the replacement of an α-hydrogen in cyclohexanone DNP (Ia) by a methoxyl group to yield *syn*-2-methoxycyclohexanone DNP (IcA) (in which the NHG group and the α-carbon are on the same side of the C═N bond) results in a bathochromic shift, $\Delta\lambda = +7$ mμ and a hyperchromic shift, $\%\ \Delta\epsilon = +4$.

TABLE III

SHIFTS IN THE ULTRAVIOLET ABSORPTION MAXIMA OF 2,4-DINITROPHENYLHYDRAZONES (DNP's) UPON SUBSTITUTION AT THE α-CARBON

The values given under each column represent the shifts in λ_{max} and in ε observed upon replacement of an α-hydrogen in the parent DNP given at the top of the column by the substituent indicated in the first column. $\Delta\lambda = \lambda^{subst}_{max} - \lambda^{unsubst}_{max}$; $\%\ \Delta\epsilon = [(\epsilon^{subst} - \epsilon^{unsubst})/\epsilon^{unsubst}]\ 100$.

Subst. X on α-carbon	Indanone (VI) Δλ, mμ (% Δε)	Tetralone (VII) Δλ, mμ (% Δε)	Benzosuberone (VIII) Δλ, mμ (% Δε)	2,3-Benzocyclooöctene-(2)-one(1) (IX)[d] Δλ, mμ (% Δε)
Br (b)	A + 1 (0)	A + 2 (+1)	B − 5 (+13)[a]	B − 4 (+7)
CH_3O (c)	A + 4 (+8)	A + 4 (+9)	B − 5 (+8)	B − 6 (−2)
AcO (d)	A − 2 (+2)	A − 1 (0)	A − 5 (−2)[b] B − 6 (−4)[b]	....
α,β-unsat. (e)	....	....	+11 (+14)[c]	+20 (+18)

[a] The replacement of an α-hydrogen in *anti*-benzosuberone DNP (VIIIaB) by a bromine atom to yield *anti*-2-bromobenzosuberone DNP (VIIIbB) results in a hypsochromic shift, $\Delta\lambda = 5$ mμ and a hyperchromic shift $\%\ \Delta\epsilon = +13$. [b] The replacement of an α-hydrogen in *syn*-benzosuberone DNP (VIIIaA) by an acetoxyl group to yield *syn*-2-acetoxybenzosuberone DNP (VIIIdA), and the replacement of an α-hydrogen in *anti*-benzosuberone DNP (VIIIaB) by an acetoxyl group to yield *anti*-2-acetoxybenzosuberone DNP (VIIIdB) results, in both cases, in very similar hypsochromic shifts ($\Delta\lambda = -5$ mμ and -6 mμ, respectively) and hypochromic shifts. [c] Relative to VIIIaB; +8(+6), relative to VIIIaA. [d] Since the configuration of IXa is not known with certainty, comparisons in this column are not free from ambiguity. The consistent values for Br- and CH_3O-substitution (*cf.* benzosuberone DNP's) could mean either that IXaA and IXaB (only one of which could be isolated) absorb at about the same place or that, if they do not, the IXa used for comparison belongs to the B-series (*cf.* footnote 12).

TABLE IV

SHIFTS IN THE ULTRAVIOLET ABSORPTION MAXIMA OF 2,4-DINITROPHENYLHYDRAZONES (DNP's) UPON SUBSTITUTION AT THE α-CARBON

The values given under each column represent the shifts in λ_{max} and in ε observed upon replacement of an α-hydrogen in the parent DNP given at the top of the column by the substituent indicated in the first column. $\Delta\lambda = \lambda^{subst}_{max} - \lambda^{unsubst}_{max}$; $\%\ \Delta\epsilon = [(\epsilon^{subst} - \epsilon^{unsubst})/\epsilon^{unsubst}]\ 100$.

Subst. X on α-carbon	Acetophenone (III) Δλ, mμ (% Δε)	Propiophenone (IV) Δλ, mμ % Δε)	Butyrophenone (V) Δλ, mμ (% Δε)
Br (b)	A − 1 (0)[a] *B − 16 (−1)	.... *B − 16 (−3)	A − 7 (−6) *B − 18 (−2)
CH_3O (c)	....	A + 5 (+5) *B − 16 (−8)	A + 3 (+6) *B − 18 (−7)
AcO (d)	A − 3 (−2)	....	....
α,β-unsat. (e)	....	+5 (+4)[b]	+6 (+8)[c]

[a] Example: the replacement of an α-hydrogen in *syn*-acetophenone DNP (IIIaA) by a bromine atom to yield *syn*-α-bromoacetophenone DNP (IIIbA) results in a very slight ($\Delta\lambda = -1$ mμ) hypsochromic shift, and no change in ε. * Values marked with an asterisk represent comparisons between a parent-DNP and a substituted DNP belonging to *opposite* configurations. [b] Relative to IVaA. [c] Relative to VaA.

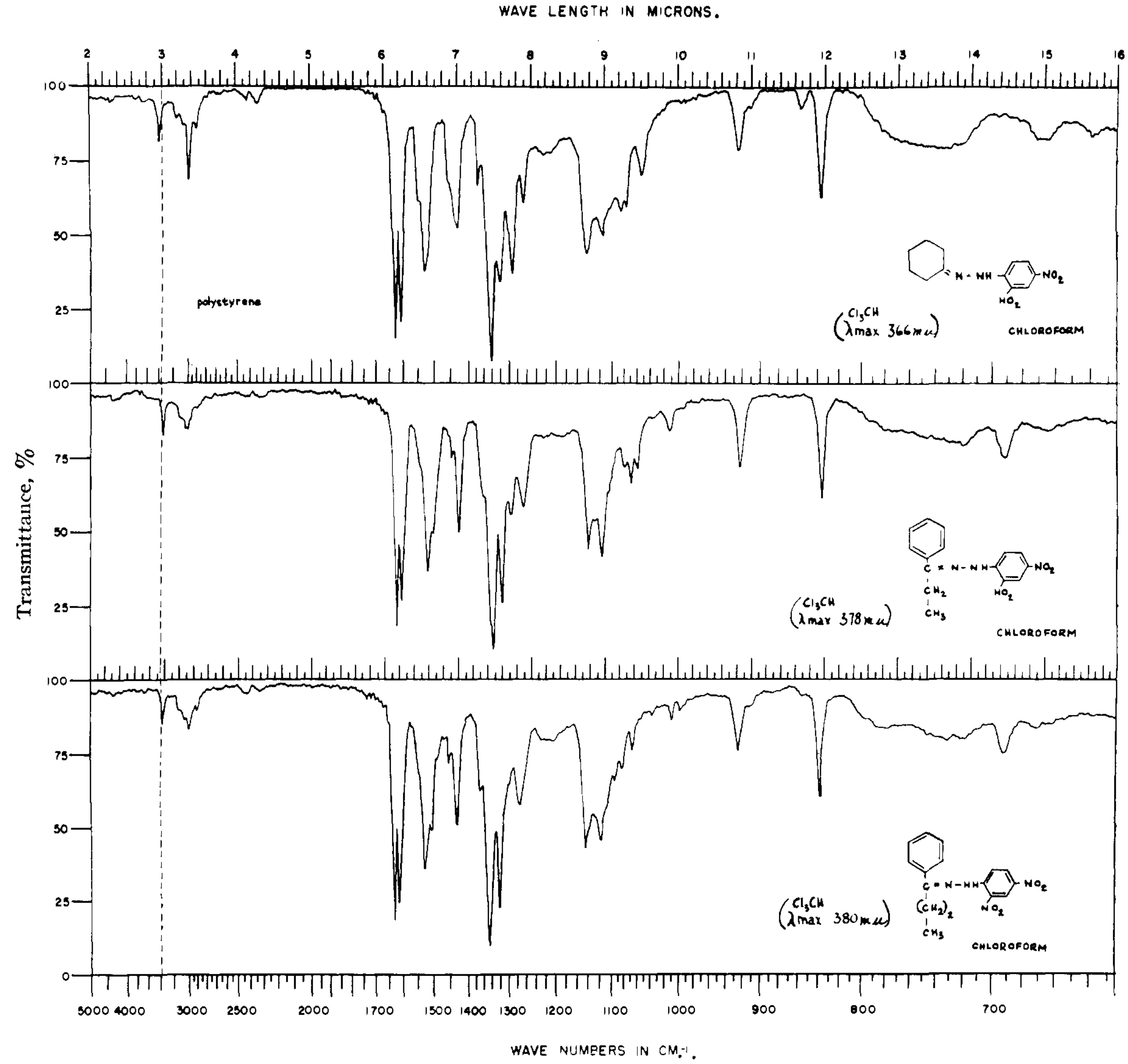


Fig. 3.

(3) The third criterion used in the configurational assignments was based on the observation that those *anti*-DNP's having an aromatic ring conjugated to the hydrazone group exhibited a second and weaker absorption maximum at *ca.* 258–260 mμ (log ε 4.0–4.1). This second maximum was absent in the isomeric *syn*-DNP's. This, then, became confirmatory evidence for the configurations assigned although in no case was it used as the sole basis for the assignment.

Using the arguments described above, in conjunction with the spectral data presented in detail in Parts I and II[9] of this study, it has been possible to assign configurations to most of the DNP's encountered in this work.[12] The results are summarized in Tables I–IV.

Ultraviolet Absorption Spectrum of 2,4-Dinitrophenylhydrazones.—Having assigned configurations to most of the DNP's, it became possible to undertake a correlation between the structure and geometry of the DNP's on the one hand, and their ultraviolet absorption spectrum on the other hand. The results of such correlation are presented in Tables I–IV. Prior to a discussion of these tables two points should be emphasized.

(1) Unless otherwise specified, comparisons between a substituted DNP and the corresponding parent (unsubstituted) DNP refer to structures having the same configuration about the C=N bond. This permits an unequivocal assessment of the effect of substitution at the α-carbon on the ultraviolet spectrum of DNP's, *within a given stereochemical series.*

(2) Whenever one isomeric form of a parent (unsubstituted) DNP and the two isomeric substituted DNP's were at hand, the shifts in absorption max-

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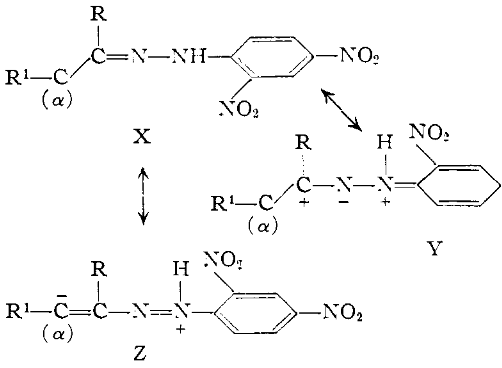
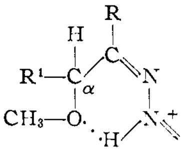
(12) The following cases appear to be ambiguous and are not assigned definite configurations: 2,2-dimethylcyclohexanone DNP (IIa), 2,3-benzocycloöctene(2)-one(1) (IXa), α-phenylpropionaldehyde DNP (XIa) and α-phenylacetone DNP (XIIa). From its spectral similarity with cyclohexanone DNP (Ia), IIa is probably *syn* (in which there is no CH_3–NHG interference). By comparison with XIcB and XIIcB, respectively, XIa and XIIa are probably *anti.* Since its ultraviolet spectrum lacks a maximum at *ca.* 260 mμ, IXa is probably *syn;* here, however, the effect of the conjugated aromatic ring is probably of little significance in either of the two isomers, and no definite assignment is warranted (*vide infra*).

ima were calculated for both cases. Evidently, one of these values (marked with an asterisk in the tables) will represent the combined effects of substitution and configurational change. For example, with reference to Table IV, a bromine atom is seen to replace an α-hydrogen of *syn*-acetophenone DNP (IIIaA) with little effect to give the bromo-DNP of the same configuration, *i.e.*, *syn*-α-bromoacetophenone DNP (IIIbA) ($\Delta\lambda = -1$ mμ). On the other hand, when the replacement of the α-hydrogen by bromine is accompanied by a change in configuration about the C=N bond to give *anti*-α-bromoacetophenone DNP (IIIbB), a relatively large hypsochromic shift is noted ($\Delta\lambda = -16$ mμ). The same observations can be made in the case of butyrophenone DNP (VaA). This emphasizes the need of taking into consideration stereochemical factors when correlating structure and ultraviolet absorption spectrum in the DNP series.[13]

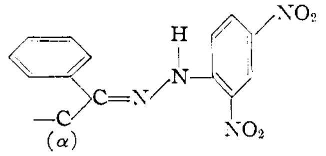
The question of the origin of the singularities in the ultraviolet spectra of DNP's brought out in Tables I–IV is of interest. A consistent picture is provided by an extension of views previously advanced[2] and discussed in terms of structures X, Y and Z.



Thus, a bathochromic shift in the ultraviolet absorption maxima of DNP's would result from a stabilization of the excited state due to increased contributions of forms such as Y. This effect was indeed observed in the following cases: (i) when, in general formula X, R = aryl was compared to R = alkyl; (ii) when a double bond was placed in position α,β (conjugated to the hydrazone group) as compared to the corresponding saturated DNP; (iii) when a methoxyl group was placed on an α-carbon, *on the same side of the C=N bond* as the NH- group of the DNP (*i.e.*, in a *syn*-configuration). In this case the effect on the absorption maximum relative to the parent (unsubstituted) DNP is small but significant. This effect is attributable to the stabilization of the excited state as a result of the hydrogen bonding interaction[14] assumed to be responsible for the shift of the N–H stretching band observed in the infrared absorption spectra of *syn*-methoxy-DNP's.



A hypsochromic shift in the ultraviolet absorption maxima of DNP's would be the result of a steric inhibition of resonance[15] affecting the excited state (through forms Y). Such effect would presumably be observed in the *anti*-isomer (series B) of a pair of isomeric DNP's having an aromatic ring conjugated to the hydrazone group (formulas III to IX of Chart I). In the *anti*-isomer, as defined here, the aromatic ring and the NHC_6H_3-2,4-$(NO_2)_2$ group are on the same side of the C=N bond where steric interference preventing effective coplanarity is possible. In other words, in the *anti*-isomer one might expect similar spectral characteristics as those of non-aromatic DNP's. This was found to be the case.



anti-isomer

A steric inhibition of resonance affecting forms such as Y, and operating *in both geometrical isomers* of the same DNP seems capable of explaining the observed ultraviolet absorption spectra of the *syn*- and *anti*-forms of benzosuberone DNP (VIIIaA and VIIIaB, respectively) when these are compared with the spectrum of tetralone DNP (VIIa) (see Table I). The geometry of the benzosuberone DNP molecule—in either the *syn*- or the *anti*-form—appears to be such as to interfere with the resonance implied by form Y. Fisher–Hirshfelder–Taylor models (Fig. 1) disclose that while in tetralone DNP (VIIa) the aromatic ring and the C=N can attain coplanarity, this is no longer possible as the size of the alicyclic ring increases to that of benzosuberone DNP (VIIIa)[16] and 2,3-benzocyclooctene(2)-one(1) DNP (IXa). The striking effect observed in comparing the ultraviolet spectra of cyclohexanone DNP (Ia) and 2,3-benzocyclooöctene-(2)-one(1) DNP (IXa) (Table I) finds a reasonable explanation on this basis.

A hypsochromic shift would also result from sta-

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[13] It should be noted that *anti*-α-bromopropiophenone DNP (IVbB) and *anti*-α-bromobutyrophenone DNP (VbB) are more stable than the respective *syn*-isomers (IVbA and VbA). In fact, only one isomeric α-propiophenone DNP (the *anti*-form) could be prepared. The stability relationship is reversed in the α-bromoacetophenone DNP's (IIIb) in which the *syn*-isomer (IIIbA) is the more stable. For correlations between stability and geometry in the DNP series see Part II (ref. 9).

[14] In this connection the large bathochromic shift resulting from removal of the 2-NO_2 group in DNP's and the somewhat smaller bathochromic shift resulting from replacement of H in the NH of DNP's by alkyls is recalled. These effects were interpreted by Szmant and Planinsek[20] in terms of hydrogen bonded structures involving the NH and the 2-NO_2 group; *cf.* ref 2a.

[15] (a) Steric inhibition of resonance has been invoked to explain the hypsochromic effect observed in the series acetylcyclohexene DNP, 1-acetyl-2-methylcyclohexene-1 DNP and 1-acetyl-2-*n*-butylcyclohexene-1 DNP (E. A. Braude, E. R. H. Jones, H. P. Koch, R. W. Richardson, F. Sondheimer and J. B. Toogood, *J. Chem. Soc.*, 1980 (1949). (b) For a discussion of the effects of steric hindrance upon ultraviolet absorption spectra see *inter alia* L. N. Ferguson, "Electron Structure of Organic Molecules," Prentice-Hall, Inc., New York, N. Y., 1952, p. 286.

[16] Huisgen and Rapp (ref. 2f) have made similar observations based on one isomer of benzosuberone DNP. It should be noted that an unambiguous interpretation of this effect requires examination of both isomers of a given DNP, so as to rule out the possible hypsochromic shift due to a change in configuration about the C=N bond.

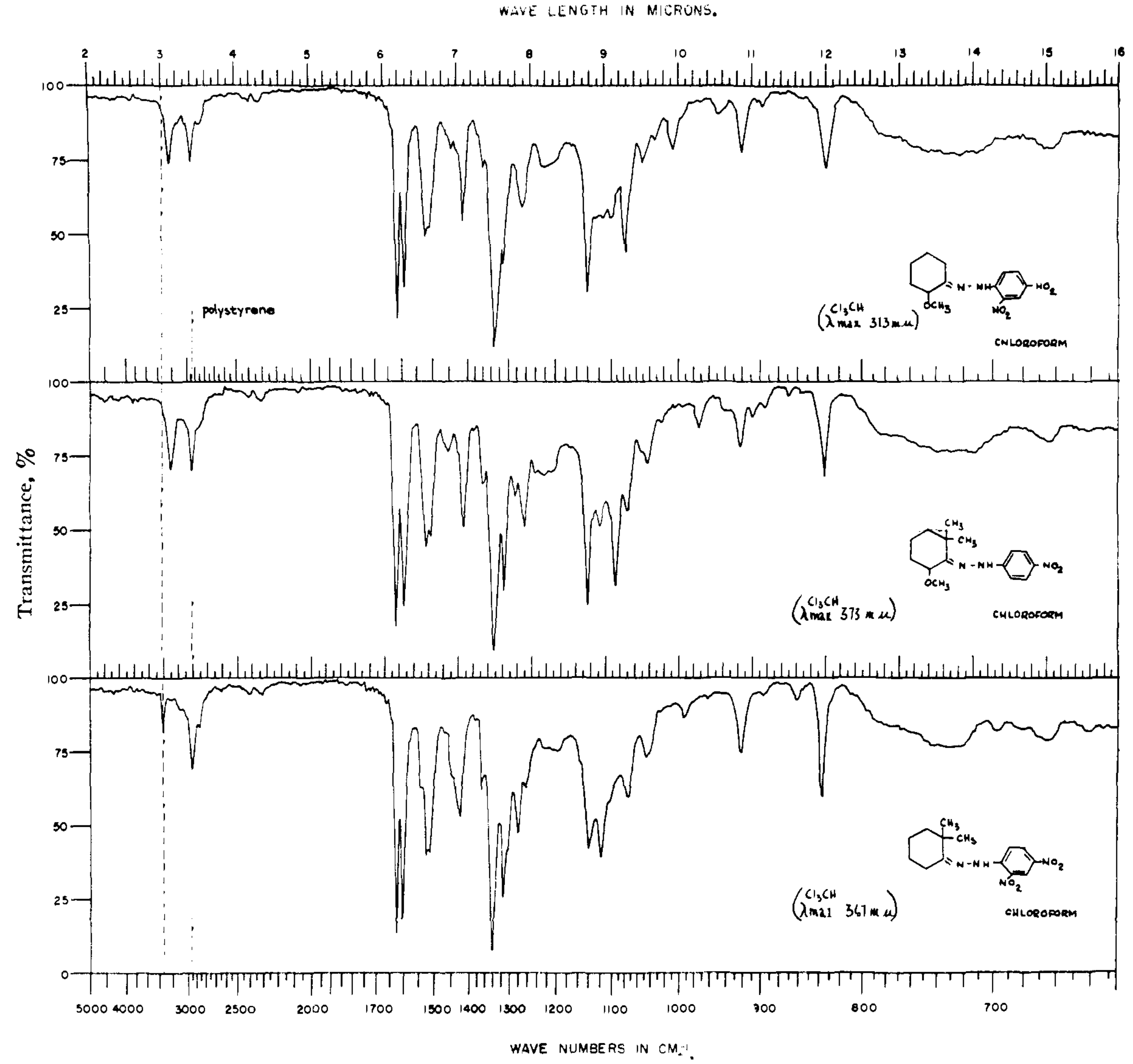

Fig. 4.

bilization of the ground state, perhaps by increased contributions of resonance forms such as Z.[17] This effect might explain the results observed when electron-attracting groups in the inductive or +I sense,[18] such as Cl, Br, CH_3O (when placed *anti* to the NH– group), and AcO are substituted in the α-carbon (relative to the unsubstituted DNP's). The acetoxyl group (AcO) is of interest since in it the hypsochromic effect is observed in both isomeric series, *i.e.*, *syn*- and *anti*-2-acetoxybenzosuberone DNP's (VIIIdA and VIIIdB) (Table III). The AcO would not be expected to participate in the hydrogen bonding relationship considered above for the CH_3O. Djerassi and Ryan[2b] have called attention to the hypsochromic effect (8 mμ) observed when a Δ^1-2-bromo-3-keto-allosteroid DNP was compared to the corresponding Δ^1-3-keto-allosteroid DNP.

α,β-Unsaturated 2,4-Dinitrophenylhydrazones.—The information concerning the configuration of the α,β-unsaturated hydrazones is of a circumstantial nature, but certain deductions appear reasonable. The significant bathochromic shift associated with the α,β-unsaturation in 6,6-dimethyl-2-cyclohexen-1-one (IIe) would seem to reflect an increased contribution of forms-Y, relative to the corresponding forms in the parent DNP, *i.e.*, 2,2-dimethylcyclohexanone DNP (IIa). The coplanarity requirements implicit in forms-Y appear on steric grounds (CH_3–NHG interference) to be more favorably fulfilled in the *syn*-configuration of IIe. The similarity between the ultraviolet spectra of 2-cyclohexen-1-one DNP (Ie) and of 6,6-dimethyl-2-cyclohexen-1-one DNP (IIe) would place Ie also among compounds in the A-series (*syn*-configuration).[19] The one isomeric form of phenyl vinyl ketone DNP (IVe) and phenyl 1-

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(17) Forms such as Z were discussed in Parts I and II[3] in connection with the lability of the halogen in α-halo DNP's.

(18) See for example M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, p. 52.

(19) DNP's of type $RCH{=}CR^1{-}C({=}N{-}NHG){-}CH_3$ of unknown configuration at both double bonds (R and R^1 are alkyl) are said[2g] to absorb in general at 377 mμ, which corresponds to the value found for Ie and IIe. Clearly, the stated generalization will hold only with a certain stereochemical series (for the olefin-DNP's of ref. 2g the *trans*-R/R^1-*anti*-NHG/C = or the *cis*-R/R^1-*anti*-NHG/C = seems favored on steric-spectral grounds).

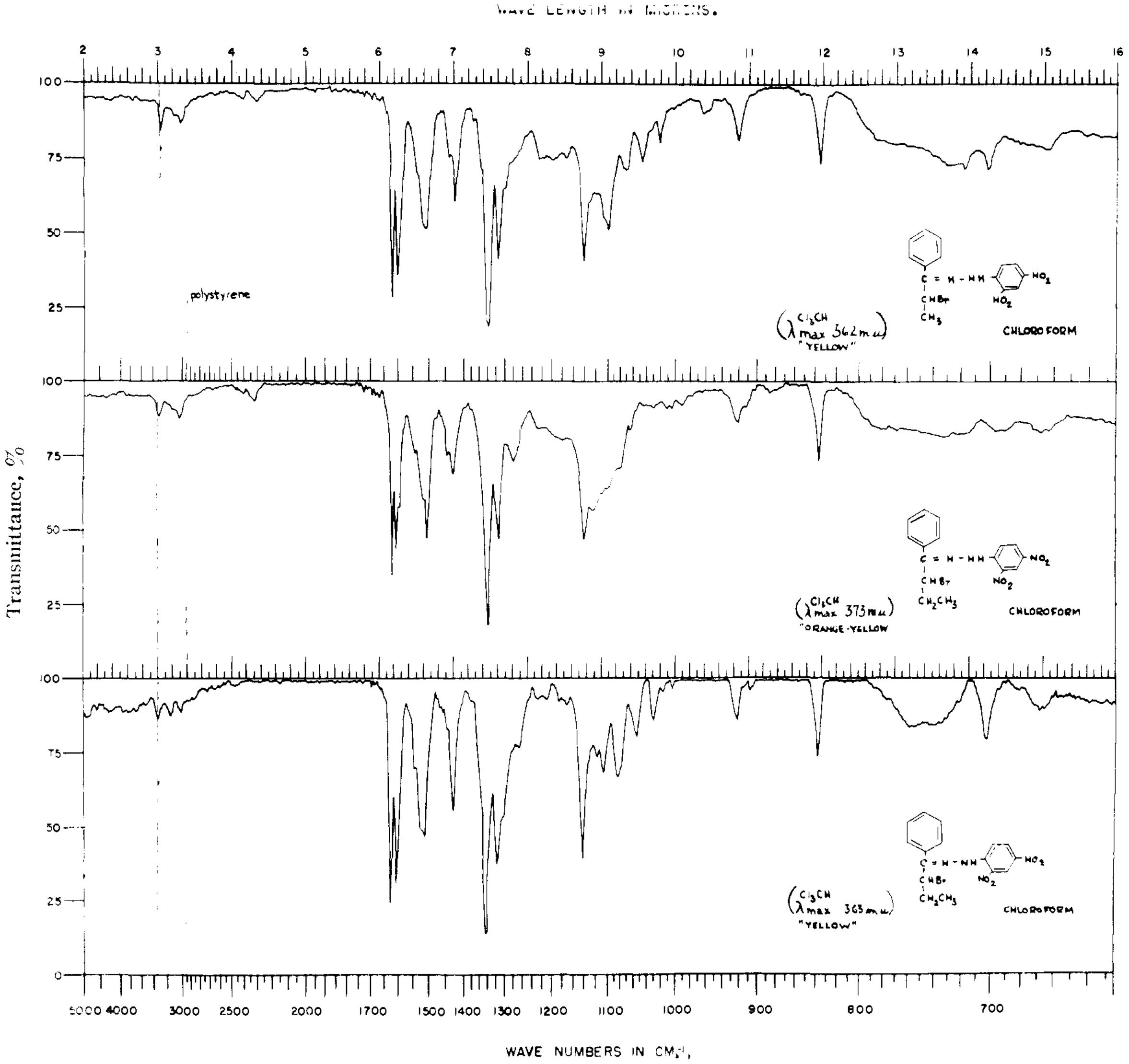

Fig. 5.

propenyl ketone DNP (Ve) which could be isolated in this work is in each case probably *syn*-, an arrangement, which in the case of unsubstituted DNP's and of α-methoxy DNP's of this type, appear to be energetically favored.[9]

The similarity between the ultraviolet absorption spectra of phenyl-1-propenyl ketone DNP (Ve) and 2,3-benzocycloöctadiene(2,7)-one(1) (IXe) suggests also a *syn*-configuration for IXe. In contrast to the unsaturated DNP's Ve and IXe, the parent saturated DNP's Va and IXa exhibited quite different spectra in the ultraviolet. This seems a consequence of the shapes of these molecules as revealed by atom models.

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