[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE A. AND M. COLLEGE OF TEXAS]

Spectrophotometric Studies of the 2,4-Dinitrophenylhydrazones of Some Dicarbonyl Compounds[1,2]

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The ultraviolet and visible spectra have been obtained for chloroform and alcoholic sodium hydroxide solutions of the 2,4-dinitrophenylhydrazine derivatives of thirteen dicarbonyl compounds. The anomalous absorption in chloroform of the mono-2,4-dinitrophenylhydrazones (DNP's) of the 1,2-dicarbonyl compounds is attributed to the electronegative acyl group which raises the excited state. The two absorption maxima exhibited by 1,2-dicarbonyl-bis-DNP's in chloroform solution are due to two excited states and the near constancy of the absorption maxima is the result of steric hindrance. The separation of two 2,4-dinitrophenylhydrazine moieties by two or more methylene groups shifts the absorption maxima to wave lengths previously associated with the DNP's of monocarbonyl compounds. Steric hindrance affects the spectra in basic solution more so than the spectra in chloroform solution.

Introduction

The spectra of the mono- and bis-2,4-dinitrophenylhydrazones (DNP's) of dicarbonyl compounds have not been studied as extensively as have the monocarbonyl derivatives.[1,4–6] Neuberg and Strauss[7] have measured the absorption maxima of three 1,2-dicarbonyl-bis-DNP's in basic solution, and, more recently, the ultraviolet and visible spectra of three mono- and four bis-DNP's in neutral and basic solutions have been described.[6c] The four-, five- and six-membered ring 1,2-dicarbonyl-bis-DNP's have also been investigated spectrophotometrically and the appearance of a band at 352 mμ attributed to the partial DNP chromophore in the *cis* configuration.[8] The ultraviolet spectra of the mono-DNP's of glyoxal and butanedione and the color developed by these derivatives in alcoholic base have been reported.[9]

This article describes results obtained from a spectrophotometric study of a series of mono- and bis-DNP's of 1,2- and 1,4-dicarbonyl compounds and the bis-DNP's of some 1,5- and 1,6-dicarbonyl compounds in neutral and basic solutions. Included are the spectra of three 1-(2,4-dinitrophenyl)-3,5-disubstituted-pyrazoles in methanol and alcoholic sodium hydroxide.

Experimental

The preparation and physical constants of the compounds used in this study have been described elsewhere.[10] The solutions were prepared at 25° by a previously described method[1] and the spectra obtained with a Beckman DK-1 recording spectrophotometer. The results are shown in Table I.

The relative insolubility of the bis-DNP's of glyoxal and pyruvaldehyde made it necessary to reflux milligram quantities in chloroform for several days. After solution was accomplished, equal volumes of chloroform were added and the solution stored at 25°. If no crystallization was observed at the end of one week, the solution was made to volume and the spectrum obtained.

The bis-*p*-nitrophenylhydrazone of glyoxal was prepared by mixing the carbonyl compound with a saturated solution of *p*-nitrophenylhydrazine in ethanol-2 *N* HCl (1:1 v./v.) and stirring for 1 hour. The filtered precipitate was washed with water until the washings were neutral and recrystallized three times from nitrobenzene to give red needles, m.p. 304–305° dec. *Anal.* Calcd. for $C_{14}H_{12}N_6O_4$: N, 25.6. Found: N, 25.6. The derivative was almost insoluble in chloroform and therefore was dissolved in acetone to obtain the spectrum [λ_{max} 439 mμ, ϵ_{max} 7.75 × 10^4]. For comparison, the spectrum of the bis-DNP of glyoxal in acetone was also obtained [λ_{max} 435, 400 (s), ϵ_{max} 4.16 × 10^4, 3.99 × 10^4(s)]. The spectra of both derivatives are shown in Fig. 1.

Results and Discussion

The absorption maxima of the 1,2-dicarbonyl-mono-DNP's in chloroform were 13 to 19 mμ less than the maxima for comparable monocarbonyl derivatives,[1] and the shift from 351 mμ for butanedione mono-DNP to 380 mμ for benzil mono-DNP is the result of conjugation to the azomethine linkage. The position of the absorption maximum of 1-phenyl-1,2-propanedione mono-DNP (356 mμ) supports the proposal that the DNP formation occurred on the 2-position of the side chain.[10]

The spectra of these derivatives indicate that the excited state is raised relative to the ground state due to the electronegative acyl group,[11] while the hydrogen bond between the acyl oxygen and the N-hydrogen, previously proposed to account for the carbonyl stretching absorption observed in the infrared spectra of these compounds,[10] results in a lowering of the ground state. In addition, these compounds can conceivably undergo tautomerism in which the N-hydrogen shifts to the carbonyl oxygen, thus producing the —N=NCR=CROH group. However, under these circumstances, the 1-phenyl-1,2-propanedione mono-2-DNP would produce a completely conjugated system and the absorption should occur at longer wave lengths than is experimentally observed. It is apparent that the tautomeric equilibria do not occur to any appreciable degree.

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(1) For the first paper of this series, see L. A. Jones, J. C. Holmes and R. B. Seligman, *Anal. Chem.*, **28**, 191 (1956).

(2) Presented before the Organic Section at the 13th Southwest Regional A.C.S. Meeting, Tulsa, Okla., December 5, 1957, and taken in part from the Ph.D. dissertation of L.A.J. submitted to the Graduate School of the A. and M. College of Texas in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1959.

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(4) *Cf.* E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 498 (1945); (b) G. D. Johnson, THIS JOURNAL, **75**, 2720 (1953); (c) H. H. Szmant and H. J. Planinsek, *ibid.*, **72**, 4042 (1950).

(5) (a) F. Ramirez and A. F. Kirby, *ibid.*, **76**, 1037 (1954); (b) J. D. Roberts and C. Green, *ibid.*, **68**, 214 (1946).

(6) (a) A. Mendelowitz and J. P. Riley, *Analyst*, **78**, 704 (1953); (b) K. Yamaguchi, S. Fukushima, T. Tabata and M. Ito, *J. Pharm. Soc.* (*Japan*), **74**, 1335 (1954); (c) C. J. Timmons, *J. Chem. Soc.*, 2613 (1957).

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(8) See F. Ramirez and R. J. Bellet, THIS JOURNAL, **76**, 491 (1954), and references cited therein.

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TABLE I

SPECTRAL CONSTANTS OF MONO-DNP'S AND BIS-DNP'S IN SOLUTION

Compound	$\lambda_{max}^{CHCl_3}$, mμ	$\epsilon_{max}^{CHCl_3}$, × 10^{-4}	$\lambda_{max}^{Alc.\ NaOH}$, mμ	$\epsilon_{max}^{Alc.\ NaOH}$, × 10^{-4}
Butanedione mono-DNP[a]	351	2.91	501	3.75
2,3-Octanedione mono-DNP	352	2.60	502	3.54
1-Phenyl-1,2-propanedione mono-DNP	356	2.60	519	4.20
Benzil mono-DNP	380	2.81	512	3.79
Glyoxal bis-DNP	391, 438	4.17, 4.43	575	6.64
Pyruvaldehyde bis-DNP	395, 435	4.35, 4.07	565	6.00
Butanedione bis-DNP	393, 435(s)	4.69, 3.97(s)	556	5.38
2,3-Octanedione bis-DNP	394, 435(s)	4.77, 3.98(s)	556	5.59
1-Phenyl-1,2-propanedione bis-DNP	400, 438	4.40, 4.11	566	5.49
Benzil bis-DNP	405, 448	4.33, 4.45	569	4.70
2,5-Hexanedione mono-DNP	362	2.22	435, 535(s)	2.34, 1.38(s)
2,5-Hexanedione bis-DNP	362	4.39	435, 535(s)	3.93, 2.45(s)
β-Methylglutaraldehyde bis-DNP	355	4.64	435, 523(s)	4.49, 2.63(s)
Glutaraldehyde bis-DNP	355	4.52	435, 523(s)	4.34, 2.59(s)
α-Hydroxyadipaldehyde bis-DNP	350	4.30	430, 500(s)	3.57, 2.02(s)
1-(2,4-Dinitrophenyl)-3,5-dimethylpyrazole	239, 325[b]	1.00, 0.721	229, 310	1.00, 0.625
1-(2,4-Dinitrophenyl)-3-methyl-5-phenylpyrazole	230, 300[b]	2.30, 0.744	239, 304	2.20, 0.781
1-(2,4-Dinitrophenyl)-3,5-diphenylpyrazole	233, 315[b]	4.01, 0.756	243, 318	4.00, 0.652

[a] Reich and Hefle (ref. 9) report butanedione mono-DNP λ_{max} 350 mμ, ϵ_{max} 2.626 × 10^4 and for glyoxal mono-DNP λ_{max} 343 mμ, ϵ_{max} 2.421 × 10^4. [b] Methanol solution.

In basic solution, the acidic N-hydrogen is removed and the excited state, requiring no separation of charge, is correspondingly lowered. The accommodation of the negative charge on the electronegative oxygen enhances the stability of the excited state,[6c] and the absorption therefore occurs at longer wave lengths, between 501 and 519 mμ.

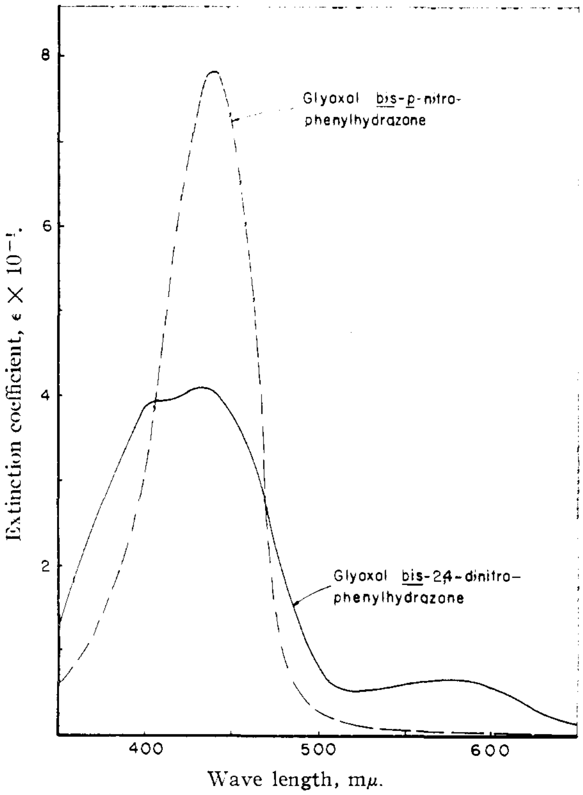
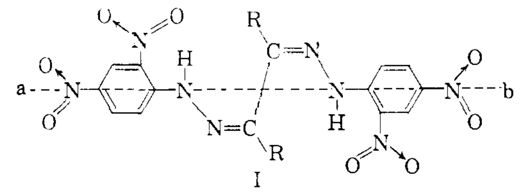


Fig. 1.—Absorption spectra of glyoxal bis-*p*-nitrophenylhydrazone and glyoxal bis-2,4-dinitrophenylhydrazone in acetone.

Previous work[8,10] and molecular models[12] show that structure I (*syn*, *syn* form) is the most reasonable structure for the bis-derivatives of 1,2-dicarbonyl compounds. (It should be noted, however, that the existence of the *anti* forms does not invalidate the following conclusions.) Free rotation about the C–C bond would be hindered due to the repulsion of the dinitrophenyl groups, and, as the size of R and R′ increase, steric hindrance to the coplanarity of the molecule would also increase. Braude and co-workers have shown that such hindrance is indicated by a hypsochromic shift of the absorption maximum and a decrease in the intensity of absorption.[13]



I

The absorption maxima of the 1,2-dicarbonyl bis-DNP's in chloroform solution remain essentially constant (band I, 391–405 mμ; band II, 435–448 mμ), independent of the groups conjugated to the C=N linkages. One possible explanation for this behavior is that steric hindrance affects the ground state more so than the excited state, hence a smaller excitation energy is required. However, the relative contributions of the steric effects to the ground and excited states must change as the size of the group changes in order to account for the constancy of the absorption. A similar proposal has been made to account for anomalous results obtained from a spectrophotometric examination of a series of symmetrical and unsym-

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(12) Catalin Products Ltd., Waltham Abbey, Essex, England.

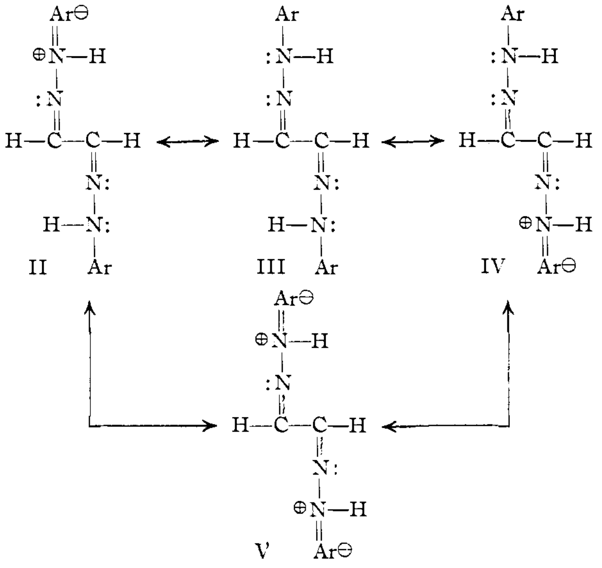
(13) (a) E. A. Braude, E. R. H. Jones, H. P. Koch, R. W. Richardson, F. Sondheimer and J. B. Toogood, *J. Chem. Soc.*, 1890 (1949); (b) E. A. Braude, F. Sondheimer and W. F. Forbes, *Nature*, **173**, 117 (1954).

metrical cyanine dyes[14] and di-N-substituted-dipyrrlymethene perchlorates.[15]

Only one band appeared in basic solution and the glyoxal derivative absorbed at the longest wave length. The benzil bis-DNP, despite the aromatic conjugation to the azomethine linkages, exhibited a hypsochromic shift of 6 mμ while the extinction coefficients decreased in the order: glyoxal < pyruvaldehyde < butanedione ≦ 2,3-octanedione ≦ 1-phenyl-1,2-propanedione < benzil. These relationships can be correlated with the increasing size of the groups R and R′ in I, clearly indicating that steric considerations are the determining factors in the spectra of these derivatives.

Considering only the co-planar glyoxal derivative and its associated resonance structures, II–V (where Ar is $2,4\text{-}C_6H_3(NO_2)_2$—and its appropriate resonance forms), II and IV correspond to two distinct but equivalent structures which could make approximately equal contributions to the excited state.

Lewis and Bigeleisen[16] have shown that when the symmetry of the crystal violet ion is decreased by suitable substitution, the single intense absorption associated with the symmetrical ion can be resolved into two separate bands, indicative of two excited states. Since the bis-*p*-nitrophenylhydrazone of gyloxal is more symmetrical about the axis ab in I than the 2,4-dinitro-derivative, a single intense absorption is observed at 439 mμ in acetone and in the same region as the glyoxal bis-DNP (Fig. 1). It is concluded that the two absorption maxima observed for the bis-DNP's of 1,2-dicarbonyl compounds represent the separation of two excited states.



The spectral data in Table I indicate that the interposition of two or more methylene groups between the respective azomethine linkages of the bis-DNP's eliminates all conjugative possibilities and the absorption maxima are located in regions previously reported for simple aldehyde and ketone DNP's.[1] The bathochromic shift observed in progressing from aldehyde to ketone derivatives has been previously attributed to the hyperconjugation of the alkyl groups adjacent to the azomethine linkage of the DNP.[17]

When 1,3-dicarbonyl compounds are treated with 2,4-dinitrophenylhydrazine the final crystalline product is a 1-(2,4-dinitrophenyl)-3,5-disubstituted pyrazole,[10,18] which exhibits a weak absorption band between 300 and 325 mμ and an intense absorption band 230–239 mμ in methanol solution (Table I). The structure of these compounds indicates that conjugation between the pyrazole and the 2,4-dinitrophenyl nucleus does not exist in the ground state. Further, for the phenyl substituted dinitrophenyl pyrazoles, although the phenyl groups are conjugated with the pyrazole ring, no bathochromic shift was apparent in either absorption maximum of the respective compounds, indicating that resonance interaction is small. The regular increase in the number of phenyl groups attached to the pyrazole ring and the extinction coefficients of the short wave length absorption suggest that this band is the result of the combined transitions occurring in the respective rings. The absorption maximum located between 300 and 325 mμ remained constant in intensity and probably is due to the nitro groups.[19] The lack of change in the absorption maxima and the extinction coefficients in basic solution further substantiate the proposal that DNP's behave as acids in basic solution and react with base by the loss of the N-hydrogen.[6c,20]

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