404. *Studies in Light Absorption. Part VII. Azines and Related Systems. A Comparison of the* –C=C– *and the* –C=N– *Chromophore.*

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The ultra-violet light absorption of some azomethine analogues of the butadiene and diphenylbutadiene systems has been determined. The replacement of one or both ethylenic by azomethine groups results in a displacement of the maxima towards shorter wave-lengths. In polyene-azines, the hypsochromic shifts (expressed as wave-number differences) with respect to the corresponding polyene-hydrocarbons are approximately independent of the length of the polyene chain and represent an increase in the excitation energy of *ca.* 3 kcals./mol. per nitrogen atom. The spectral properties of the acyclic azomethine systems are compared with those of heterocyclic nitrogen compounds.

The effect of replacing ethylenic by azomethine groups on the ultra-violet light absorption of conjugated systems is of much interest in connection with the theory of electronic spectra. It has so far been discussed mainly in relation to cyclic systems, for which a considerable amount of experimental work is now available (cf. Bowen, *Ann. Reports*, 1943, **40**, 25; Braude, *ibid.*, 1945, **42**, 105, Maccoll, *J.*, 1946, 670). The object of the present work was to compare the –C=C– and –C=N– chromophores in linear systems of the butadiene and polyene types.

There are five possible azomethine analogues of the butadiene system, of which three, namely the enimine system –C=C–C=N–, the di-imine system –N=C–C=N–, and the azine system –C=N–N=C– are readily accessible by the condensation of appropriate carbonyl compounds and primary amines. The azomethine analogues of 1 : 4-dimethylbutadiene and 1 : 4-diphenylbutadiene have been thus prepared (see Experimental section), and their light absorption data are given in Table I and Figures 1 and 2.

The introduction of one azomethine group as in *crotonylidenebutylamine* and cinnamylideneaniline results in a slight decrease in $\lambda_{max.}$ (by 70—240 A.), whilst the introduction of two azomethine groups as in diacetyldi-*N*-butylimine and diacetylanil, and as in butyraldazine and benzylideneazine, gives rise to a somewhat larger hypsochromic shift (by 190—280 A.). The characteristic bands of most of the azomethine derivatives are slightly less intense than those of the ethylenic analogues and mostly show twin maxima, whereas only diphenylbutadiene, but not dimethylbutadiene, exhibits vibrational structure in solution. The diphenyl derivatives exhibit short-wave-length in addition to their long-wave-length absorption (Fig. 2); the former is ascribed to partial chromophores and not included in Table I. In the case of diacetyldianil, the reduction in intensity of the long-wave-length band is very pronounced, and the assignment of bands cannot be regarded as certain in this case, steric or other factors associated with the presence of the two extra methyl substituents possibly intervening. Neither glyoxaldi-*N*-butylimine nor glyoxal dianil, in which these complications would not arise, could be prepared in the pure state.

Table I.*

Replacement of –C=C– *by* –C=N– *in the butadiene and the diphenylbutadiene system.*

	$\lambda_{max.}$, A.	$\varepsilon_{max.}$		$\lambda_{max.}$, A.	$\varepsilon_{max.}$
Me·CH=CH·CH=CHMe ...	2270	22,500 [1]	Ph·CH=CH·CH=CHPh ...	3280	41,000 [2]
Me·CH=CH·CH=NBu ...	2200	23,000		3500	35,000
Bu·N=CMe·CMe=NBu ...	2060	17,000	Ph·CH=CH·CH=NPh ...	3040	30,000
	2090	18,500		3250	24,800
Pr·CH=N·N=CHPr	2050	13,000	Ph·N=CMe·CMe=NPh ...	3000	2,000
	2080	11,500		3250	2,000
			Ph·CH=N·N=CHPh	3000	36,000 [3]
				3080	35,000

* Unless otherwise stated, data in this and subsequent tables are for ethanol solutions.

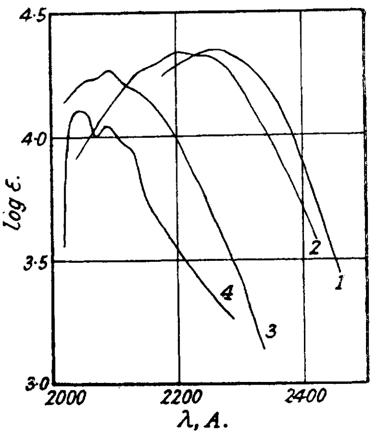
[1] Booker, Evans, and Gillam, *J.*, 1940, 1453.

[2] Hausser, Kuhn, and Smakula, *Z. physikal. Chem.*, 1935, *B*, **29**, 384; Hausser, Kuhn, and Seitz, *ibid.*, p. 391.

[3] Ferguson and Branch, *J. Amer. Chem. Soc.*, 1944, **66**, 1467, record only one maximum at 3000 A. for this compound.

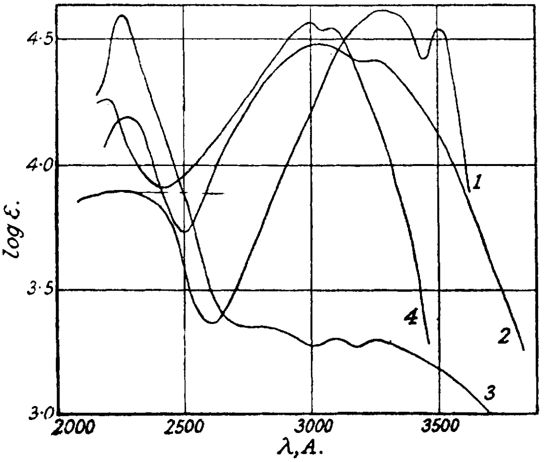
Since the effects of replacing ethylenic by azomethine groups in dimethylbutadiene and diphenylbutadiene are very similar, it was of interest to determine to what extent these effects are independent of the total length of more extended linear chromophores. This can readily be tested in the case of the azine system, where series of vinologues are known. Data for the azines of aliphatic and aromatic polyene-aldehydes, and for the corresponding polyene-hydrocarbons, are given in Table II. The hypsochromic shift due to the azine grouping increases as the absorption maxima move towards the visible region with increasing numbers of conjugated groups, but the frequency (wave-number) differences remain reasonably constant at about 2100 cm.$^{-1}$ per azine grouping, with the exception of the first member, acetaldazine, where $\Delta(1/\lambda) = 4030$ cm.$^{-1}$ A wave-number difference of 2100 cm.$^{-1}$ represents an energy difference of 6·0 kcals./mol., or 3·0 kcals./mol. per nitrogen atom. It thus appears that the excitation energy involved in the electronic transition associated with the long-wave-length bands is increased by about 3 kcals./mol. by the replacement of an ethylenic by an azomethine group, independently of the total length of the polyene chain.

FIG. 1.



Light absorption in ethanol of
(1) Me·CH:CH·CH:CHMe,
(2) Me·CH:CH·CH:NBu,
(3) Bu·N:CMe·CMe:NBu,
(4) Pr·CH:N·N:CHPr.

FIG. 2.



Light absorption in ethanol of
(1) Ph·CH:CH·CH:CHPh,
(2) Ph·CH:CH·CH:NPh,
(3) Ph·N:CMe·CMe:NPh,
(4) Ph·CH:N·N:CHPh.

TABLE II.

Replacement of –C=C– *by* –C=N– *in polyene systems.*

	X = CH.		X = N.*		$\Delta(1/\lambda)$,
	$\lambda_{\max.}$	$\varepsilon_{\max.}$	$\lambda_{\max.}$	$\varepsilon_{\max.}$	cm.$^{-1}$.†
$(\mathrm{Me{\cdot}CH{=}X})_2$	2270	25,000	2080	10,000	4030
$(\mathrm{Me{\cdot}CH{=}CH{\cdot}CH{=}X})_2$	2960	52,000 [1]	2770	36,000	2320
$(\mathrm{Me{\cdot}CH{=}CH{\cdot}CH{=}CH{\cdot}CH{=}X})_2$	3600	70,000 [1]	3380	73,000	1810
$(\mathrm{Me{\cdot}CH{=}CH{\cdot}CH{=}CH{\cdot}CH{=}CH{\cdot}CH{=}X})_2$	4200	36,000 [1]	3850	84,000	2160
$(\mathrm{Ph{\cdot}CH{=}X})_2$	3280	41,000 [2]	3040	36,000	2400
$(\mathrm{Ph{\cdot}CH{=}CH{\cdot}CH{=}X})_2$	3750	90,000 [2]	3500	65,000 [3]	2080
$(\mathrm{Ph{\cdot}CH{=}X{\cdot}X{=}CH})_2$	,,	,,	3200 ‡	42,000	2290
$(\mathrm{Ph{\cdot}CH{=}CH{\cdot}CH{=}CH{\cdot}CH{=}X})_2$	4200	117,000 [2]	3850	48,000 [3]	2160

[1] Kuhn and Grundmann, *Ber.*, 1938, **71**, 442; Blout and Fields, *J. Amer. Chem. Soc.*, 1948, **70**, 189.

[2] Hausser, Kuhn, and Smakula, *loc. cit.*

[3] Ferguson and Branch, *loc. cit.*

* Since the completion of this work, data for the aliphatic polyene-azines, though under different solvent conditions, have been published by Blout and Fields, *loc. cit.*

† Calculated from data for dibenzylidenediacetyl dihydrazone, assuming the hypsochromic effect of the methyl groups to be similar to that in related systems (see Table III).

‡ Per azine grouping.

A striking difference in the properties of the butadiene system and its azomethine analogues is revealed by the effect of alkyl substitution (Table III). In butadiene and its derivatives, each alkyl substituent attached to the chromophoric system results in a bathochromic shift of about 50 A. (Woodward, *J. Amer. Chem. Soc.*, 1941, **63**, 1123). The effect of alkyl substituents in the enimine system can be derived by comparing the data for crotonaldehyde oxime and mesityl oxide oxime (Evans and Gillam, *J.*, 1943, 565). Crotonaldehyde oxime exhibits a maximum at slightly longer wave-length (2295 A.) than crotonylidenebutylamine (2200 A.), in accordance with the usual greater auxochromic effect of hydroxyl as compared with alkyl substituents (cf. Part III, *J.*, 1946, 948), but there is hardly any further displacement of the maximum in mesityl oxide oxime, which has two additional methyl groups attached to the chromophoric system. A similar insensitivity to alkyl substitution is observed in other enimine derivatives, such as semicarbazones, containing the chromophoric grouping $\mathrm{-C{=}C-C{=}N\cdot NH\cdot COMe}$ (Evans and Gillam, *loc. cit.*). It might perhaps be expected that the properties of the $\mathrm{-C{=}C-C{=}N-}$ chromophore would be intermediate between those of the $\mathrm{-C{=}C-C{=}C-}$ and $\mathrm{C{=}C-C{=}O}$ chromophores. However, this is evidently not the case. Whereas the enimine analogue, crotonylidenebutylamine, absorbs maximally at a lower wave-length than dimethylbutadiene, the enone analogue, pent-3-en-2-one, absorbs at a higher wave-length ($\lambda_{\max.}$ 2240 A.) and, whereas alkyl substitution is almost without effect in the enimine system, its effect in the enone is even greater than in the diene system (Evans and Gillam, *J.*, 1941, 815).

TABLE III.

The effect of methyl substituents in azomethine systems.

	$\lambda_{\max.}$, A.	$\varepsilon_{\max.}$	$\Delta\lambda$, A.
$\mathrm{Me\cdot CH{=}CH\cdot CH{=}N\cdot OH}$	2295	16,900 [1]	—
$\mathrm{Me\cdot CH{=}CMe\cdot CMe{=}N\cdot OH}$	2305	17,800 [1]	+ 10
$\mathrm{HO\cdot N{=}CH\cdot CH{=}N\cdot OH}$	2360 2420	17,600 15,400	— —
$\mathrm{HO\cdot N{=}CMe\cdot CMe{=}N\cdot OH}$	2270	18,000	−90
$\mathrm{Ph\cdot CH{=}N\cdot N{=}CHPh}$	3000	28,000	—
$\mathrm{Ph\cdot CMe{=}N\cdot N{=}CMePh}$	2650 2700	20,500 20,500	−300 —
$p\text{-}\mathrm{MeO\cdot C_6H_4\cdot CH{=}N\cdot N{=}CH\cdot C_6H_4\cdot OMe}\text{-}p'$	3310	47,000	—
$p\text{-}\mathrm{MeO\cdot C_6H_4\cdot CMe{=}N\cdot N{=}CMe\cdot C_6H_4\cdot OMe}\text{-}p'$	3030	28,000	−270

[1] Evans and Gillam, *J.*, 1943, 565.

TABLE IV.

The effect of nuclear substituents in the benzylideneazine system,
$\mathrm{C_6H_3RR'\cdot CH{=}N\cdot N{=}CH\cdot C_6H_3RR'}$.

R.	R′.	$\lambda_{\max.}$, A.	$\varepsilon_{\max.}$	$+\Delta\lambda$, A.
H	H	3000, 3080	36,000, 35,000	—
o-Cl	H	3070	36,000	70
m-Cl	H	3000, 3150, 3230	38,500, 33,000, 18,000	0
p-Cl	H	3100, 3220	40,000, 36,000	100
o-OH	H	2950, 3540	30,000, 25,500	540
m-OH	H	2980, 3060, 3300	28,500, 28,000, 21,500	60
p-OH	H	3350	44,000	350
o-OH	*p*-OH	3070, 3670, 3750	12,000, 42,500, 39,000	670
o-OMe	H	2820, 2910, 3390	17,000, 18,000, 28,000	390
p-OMe	H	3300	36,000	300
m-OMe	*p*-OMe	3430	43,500	430
m-OMe	*p*-OH	3470	42,000	470
p-$\mathrm{NMe_2}$	H	3220, 4000	11,000, 63,000	1000

In the di-imine system, comparing the data for glyoxime and dimethylglyoxime, the introduction of two methyl substituents actually results in a *decrease* in $\lambda_{\max.}$ (by about 100 A.). An even more pronounced hypsochromic shift (by about 300 A.) occurs in the azine system, as shown by the data for benzylideneazine and phenyl methyl ketazine, and their *pp′*-dimethoxy-derivatives. Since the methyl substituents would not be expected to prevent a coplanar configuration of either the glyoxime or the benzylideneazine systems (cf. Blout, Eager, and Gofstein, *J. Amer. Chem. Soc.*, 1946, **68**, 1983), this effect is unlikely to be a steric one of the type discussed in Part VI (preceding paper), but is presumably conditioned by the electronic properties of the azomethine group.

In contrast to the somewhat unexpected hypsochromic effect of methyl substituents attached directly to the di-imine or azomethine systems, the effect of nuclear substituents in benzylideneazine is the expected bathochromic one, increasing in the order $\mathrm{Cl < OH < OMe < NMe_2}$, as in other conjugated systems of this type (cf. Part III, *loc. cit.*) (Table IV). The displacements are least for *m*- and largest for *p*-substituents, whilst *o*-substituents often cause the splitting of the long-wave-length bands into two subsidiary bands. This effect has already been observed and interpreted by Blout and Gofstein (*J. Amer. Chem. Soc.*, 1945, **67**, 13) with whose data our own are in reasonably good agreement as far as they overlap.

The hypsochromic effect produced by replacing ethylenic by azomethine groups may be compared with the corresponding effects observed in cyclic conjugated systems (Table V). Such a comparison can be of only limited significance since the long-wave-length bands exhibited by the cyclic systems are of low intensity and therefore due to " forbidden " transitions not analogous to those responsible for the long-wave-length absorption of the open-chain analogues (cf. Sklar, *J. Chem. Physics*, 1937, **5**, 669; Mulliken, *ibid.*, 1939, **7**, 353). However, the high-intensity bands in the 2400—2800 A. region are probably comparable, and it will be seen that, in contrast to the behaviour of open-chain systems, the introduction of a nitrogen atom produces only small and irregular changes in $\lambda_{max.}$ not exceeding 100 A. in the series pyridine, pyrimidine, and pyrazine; naphthalene, quinoline, and *iso*quinoline; and anthracene, acridine, and phenazine. The pronounced bathochromic effect observed in six-membered heterocyclic compounds containing two or more *adjacent* nitrogen atoms (*e.g.*, pyridazine, tetrazine) is probably different in origin and arises from the incursion of Kekulé structures involving $-N{=}N-$ links (cf. Maccoll, *loc. cit.*).

The theoretical interpretation of the empirical relations outlined in this paper will be discussed in a separate communication.

TABLE V.

Replacement of $-C{=}C-$ *by* $-C{=}N-$ *in cyclic systems.*

	$\lambda_{max.}$, A.	$\varepsilon_{max.}$	$\lambda_{max.}$, A.	$\varepsilon_{max.}$
Benzene	2550	250 [5]	—	—
Pyridine	2500	2,000 [5]	—	—
Pyrimidine	2430	3,000	2750	300 [2]
Pyrazine	2600	5,200	3110	580 [1]
Naphthalene	2760	7,900	3110	345 [3]
Quinoline	2750	4,500	3110	6300 [3]
*iso*Quinoline	2620	3,700	3180	3550 [3]
Anthracene	2500	160,000	3800	630 [4]
Acridine	2500	160,000	3600	1000 [4]
Phenazine	2500	120,000	3700	1600 [4]

[1] This paper.
[2] Heyroth and Loofbourow, *J. Amer. Chem. Soc.*, 1934, **56**, 1728 (in water).
[3] Morton and de Gouveia, *J.*, 1934, 911 (in hexane).
[4] Radulescu and Ostrogovich, *Ber.*, 1931, **64**, 2233.
[5] Menczel, *Z. physikal. Chem.*, 1927, **125**, 161 (in hexane).

EXPERIMENTAL.

Light-absorption Measurements.—Measurements in the region above 2200 A. were made with a Hilger medium spectrograph and Spekker photometer, as previously described (Part I, *J.*, 1945, 490). Absorption curves extending to the region below 2200 A. were determined with a Beckman DU quartz photoelectric spectrophotometer, Serial No. 1623, using 1 cm. quartz cells.

Materials.—Solids were crystallised from ethanol unless otherwise stated. Light-absorption data are given when not, or only partly, included in Tables I—V or Figures 1 and 2, and refer to solutions in ethanol unless otherwise stated. The following compounds are known. Acetaldazine (Curtius and Zinkeisen, *J. pr. Chem.*, 1898, **58**, 325), prepared by slowly adding 50% aqueous hydrazine hydrate (8 ml.) to freshly distilled acetaldehyde (11·3 ml.) at $-5°$, and extracting the mixture with ether, distilled as a colourless liquid, b. p. 95—96°, which very rapidly becomes yellow when kept. The light absorption is similar to that of butyraldazine (see below), but acetaldazine is very much less stable. Crotonaldazine (Hladik, *Monatsh.* 1903, **24**, 438), m. p. 98°. Sorbaldazine (Kuhn and Hoffer, *Ber.*, 1930, **63**, 2164), m. p. 170°, max. 2600 and 3380 A., ε 9200 and 73,000, respectively. Octatrienaldazine (*idem, ibid.*), m. p. 220—222° (from *n*-butanol), max. 2440, 2510, and 3850 A., ε 12,000, 12,000, and, 84,000, respectively. Benzylideneazine (Curtius and Jay, *J. pr. Chem.*, 1889, **39**, 44), m. p. 96°. 2 : 2'- (*idem, ibid.*), m. p. 214°, 3 : 3'- (Franzen and Eichler, *ibid.*, 1910, **82**, 247), m.p. 208—209°, and 4 : 4'-Dihydroxybenzylideneazine (Knopfer, *Monatsh.*, 1909, **30**, 31), m. p. 268°. 2 : 4 : 2' : 4'-Tetrahydroxybenzylideneazine (*idem, ibid.*), m. p. 320°. 2 : 2'- (Vorlander, *Ber.*, 1906, **39**, 807), m. p. 141°, and 4 : 4-Dimethoxybenzylideneazine (Knopfer, *loc. cit.*), m. p. 170—172°. 3 : 4 : 3' : 4'-Tetramethoxybenzylideneazine (Gattermann, *Annalen*, 1907, **357**, 668), m. p. 193—194° (from benzene). 4 : 4'-Dihydroxy-3 : 3'-dimethoxybenzylideneazine (Knopfer, *loc. cit.*), m. p. 195°. 2 : 2'- (Curtius and Pauli, *Ber.*, 1901, **34**, 849), m. p. 141°, 3 : 3'- (Curtius and Melsbach, *J. pr. Chem.*, 1910, **81**, 536), m. p. 140°, and 4 : 4'-Dichlorobenzylideneazine (Pascal and Normand, *Bull. Soc. chim.*, 1911, [iv], **9**, 1061), m. p. 208° (from benzene). 4 : 4'-Bisdimethylaminobenzylideneazine (Knopfer, *loc. cit.*), m. p. 261—262°. 2-Naphthylideneazine (Gattermann, *Annalen*, 1913, **393**, 228), m. p. 235°, max.: 2730, 2880, and 3300 A., ε 59,000, 49,500, and 69,000, respectively, inflexion

3600 A., ε 43,000. Phenyl methyl ketazine (Knopfer, *loc. cit.*), m. p. 121—122°, max.: 2650 and 2700 A., ε 20,500 and 20,500, respectively, inflexions 2780 and 2920 A., ε 19,500 and 17,000, respectively. Cinnamaldehyde anil (Doebner and Miller, *Ber.*, 1883, **16**, 1665), m. p. 109°. Diacetyldianil (Pechmann, *Ber.*, 1888, **21**, 1415), m. p. 136°. 4 : 4′-Bisdimethylamino glyoxaldianil (Pechmann and Schmitz, *Ber.*, 1898, **31**, 294), m. p. 256—257° (from xylene), maxima 2550, 3080, and 4600 A., ε 18,300, 5900, and 35,300, respectively. Dibenzylidenediacetyl dihydrazone (Darapski and Spannagel, *J. pr. Chem.*, 1915, **92**, 272), m. p. 125°, max.: 2230 and 3090 A., ε 17,000 and 42,000, respectively. Glyoxime, m. p. 179° (from water). Dimethylglyoxime, m. p. 246°. Pyrazine, m. p. 50° (distilled), kindly furnished by Professor F. S. Spring, had max.: 2560, 2600, 3110, and 3160 A., ε 4800, 5200, 580, and 560, respectively, inflexion 2660 A., ε 4000 (in ethanol), and maxima 2560, 2600, 3100, 3160, 3210, and 3270 A., ε 4550, 4700, 560, 700, 800, and 840, respectively, inflexion 2650 A., ε 3900 (in *cyclo*hexane).

The following are new:

n-*Butyraldazine*.—The azine was prepared from freshly distilled butyraldehyde, using the procedure described for acetaldazine, and distilled as a pale yellow oil, b. p. 186—188° (Found: C, 68·3; H, 11·3; N, 20·3%; *M*. in camphor, 133. $C_8H_{16}N_2$ requires C, 68·6; H, 11·4; N, 20·0%; *M*, 140). The azine has been previously prepared by Taipolie (*J. Russ. Phys. Chem. Soc.*, 1925, **57**, 506), but no details are given by this author.

Crotonylidenebutylamine.—Freshly distilled crotonaldehyde (14 g.) was added to *n*-butylamine (13·2 g.) during 30 minutes at −10° with vigorous stirring. The product was treated with an excess of solid potassium hydroxide and fractionated from fresh potassium hydroxide (cf. Tiollais, *Bull. Soc. chim.*, 1947, **14**, 708). The *imine* distilled as a pale yellow oil, b. p. 162—164°, $n_D^{23°}$ 1·4595 (Found: C, 76·5; H, 12·05; N, 11·6. $C_8H_{15}N$ requires C, 76·8; H, 12·0; N, 11·2%).

Diacetyldi-N-*butylimine*.—Diacetyl (7·6 g.) was added to *n*-butylamine (13·2 g.) over 1 hour at 0°. The mixture was stirred for a further 30 minutes at room temperature and then treated with an excess of anhydrous sodium sulphate. The *di-imine* distilled as a colourless liquid, b. p. 123—124°/17 mm., $n_D^{20°}$ 1·4610 (Found: C, 73·1; H, 12·1; N, 13·9. $C_{12}H_{24}N_2$ requires C, 73·5; H, 12·2; N, 14·3%). It rapidly becomes yellow on contact with air.

Benzylidenefurfurylideneazine.—A solution of furfuraldehyde (4·8 g.) and benzylidenehydrazine (6 g.) in absolute ethanol (15 ml.) was heated under reflux for 15 minutes. After the mixture had been cooled and diluted with a little water, the *azine* separated and crystallised from ethanol in needles, m. p. 63—64° (Found: C, 72·9; H, 5·2; N, 14·6%. $C_{12}H_{10}N_2$ requires C, 72·7; H, 5·1; N, 14·2%). Max. 3120 and 3240 A.; ε 3600 and 3400, respectively.

4 : 4′-*Dimethoxyphenyl Methyl Ketazine*.—The *azine* separated on adding a solution of *p*-methoxyacetophenone (7·5 g.) in ethanol (70 ml.) to a warm solution of hydrazine sulphate (3·25 g.) and sodium carbonate (2·65 g.) in water (75 ml.). It crystallised from benzene in needles, m. p. 200·5° (Found: C, 72·9; H, 6·9; N, 9·2. $C_{18}H_{20}O_2N_2$ requires C, 73·0; H, 6·8; N, 9·5%).

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