Nuclear Magnetic Resonance Spectra of Azomethines. Part I. Benzylideneanilines

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N.m.r. spectra of 28 azomethines of the type $Ar^1CH{=}NAr^2$ have been measured in deuteriochloroform. Susbtituent and steric effects on the chemical shift of the aldimine proton are discussed. *ortho*-Substitution in the aldehyde ring has a deshielding effect on this proton whereas *ortho*-substitution in the amine ring is shielding. The CH=N group causes a downfield shift of *ca.* 0.60 p.p.m. for aromatic protons *ortho* to the carbon.

IN connection with another problem, information was required about (1) substituent effects (including steric factors) on the chemical shift of the azomethine proton in compounds of the type $Ar^1CH{=}NAr^2$, where both aryl groups are substituted benzenes, and (2) the effects of the CH=N group on the chemical shifts of the protons in the two rings. Earlier n.m.r. studies [1,2] of aromatic azomethines have been mainly concerned with hydrogen bonding between the nitrogen and a nearby hydroxy-group but Tabei and Saitou [3] attempted to correlate substituent effects on the chemical shift of the azomethine proton with Hammett's σ_p constants and showed that some correlation exists for *para*-substituents in the aldehydic ring but not for those in the amine ring, where indeed *para*-substituents, apart from NMe_2, have only a small effect. Tabei and Saitou attribute the latter result to non-planarity of the NAr^2 and $Ar^1CH{=}N$ parts of the molecule, resulting from twisting about the nitrogen–carbon single bond, for which there is considerable evidence from studies of electronic spectra [4-11] and from *X*-ray crystal analysis.[12]

Our present studies of the n.m.r. spectra of azomethines (1)—(28) confirm that *para*-substitution in the aldehyde aromatic ring produces changes in the chemical shift of the azomethine proton (Table 1) which are in line with the conjugative effects of the substituents.

$$Ar^1\,CH{=}NAr^2 \quad (1)\text{—}(28)$$

Thus the electron-withdrawing effect of the *p*-nitro-group results in a downfield shift of *ca.* 0.12 p.p.m. and the electron-releasing effect of a *p*-dimethylamino- or a *p*-methoxy-group in upfield shifts of *ca.* 0.14 and *ca.* 0.07 p.p.m. respectively. In our compounds and in all but one of those investigated by Tabei and Saitou, *para*-substitution in the aniline ring has a smaller effect ($\ngtr$ 0.05 p.p.m.) on the chemical shift of the azomethine proton. The only exception is the *p*-dimethylamino-group which results in a downfield shift of 0.09 p.p.m.[3] Bürgi and Dunitz [12] found that in the crystal the aniline ring is twisted out of the C–N=C–C plane by 55° in

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[10] V. I. Minkin, Yu. A. Zhdanov, E. A. Medyantzeva, and Yu. A. Ostroumov, *Tetrahedron*, 1967, **23**, 3651.

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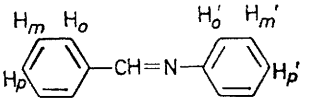
benzylideneaniline and by 50° in *p*-methylbenzylidene-*p*-nitroaniline; the similarity of crystal reflectance spectra and solution electronic spectra makes it very likely that the molecules in solution have similar geometries in their most stable conformations. With such angles of twist, conjugation between the aniline ring and the carbon–nitrogen double bond is not totally prohibited but will be considerably reduced and it is probable that the deshielding effect of the *p*-dimethylamino-group on the azomethine proton is due to the dominance of the inductive effect of this substituent over its partially suppressed conjugative effect. *p*-Methoxy also has a (marginally) deshielding effect.

ortho-Substituents in the aldehyde ring have a marked deshielding effect even when they are normally electron-releasing [compounds (20)—(28)]. A downfield shift of *ca.* 0.14 for hydroxy [(20)—(22)] is increased to *ca.* 0.32 p.p.m. when two *o*-methoxy-groups [(23)—and (24)] or two *o*-methyl groups [(28)] are present. Larger downfield shifts occur with *o*-nitro- or σ-bromo-substituents. In general closely similar substituent effects (for both *para*- and *ortho*-substitution) are observed in the be-

TABLE 1

Chemical shifts (δ; Me_4Si; $CDCl_3$) of aldimine, aromatic, and methyl protons in azomethines (1)—(28)



Compound	Ar¹	Ar²	CH=N	H_o	H_m	H_p	H_o'	H_m'	H_p'
(1)	Ph	Ph	8.42 [a]	7.80—7.97 (m)	7.33—7.47 (m)		7.10—7.47 (m)		
(2)	Ph	4-MeC_6H_4	8.43 [c]	7.80—7.97 (m)	7.35—7.47 (m)		7.15 (s)	7.15 (s)	2.33 (s, Me)
(3)	Ph	4-$MeOC_6H_4$	8.43 [d]	7.78—7.95 (m)	7.35—7.45 (m)		7.21 (d)	6.89 (d)	3.77 (s, OMe)
(4)	4-$O_2NC_6H_4$	Ph	8.55 [e]	8.06 (d)	8.30 (d)		7.17—7.65 (m)		
(5) [f]	4-$O_2NC_6H_4$	4-MeC_6H_4	8.53	8.03 (d)	8.27 (d)		7.18 (s)	7.18 (s)	2.37 (s, Me)
(6)	4-$O_2NC_6H_4$	4-$MeOC_6H_4$	8.55	8.03 (d)	8.28 (d)		7.29 (d)	6.94 (d)	3.83 (s, OMe)
(7) [g]	4-$O_2NC_6H_4$	2,4,6-$Me_3C_6H_2$	8.30	8.06 (d)	8.31 (d)		2.10 (s, Me)	6.89 (s)	2.28 (s, Me)
(8) [h]	4-$O_2NC_6H_4$	4-Br-2,6-$Me_2C_6H_2$	8.28	8.07 (d)	8.33 (d)		2.10 (s, Me)	7.20 (s)	
(9) [i]	4-$O_2NC_6H_4$	2,6-$Cl_2C_6H_3$	8.47	8.11 (d)	8.34 (d)			6.85—7.43 (m)	
(10)	4-$Me_2NC_6H_4$	Ph	8.28 [j]	7.74 (d)	6.68 (d)	2.98 (s, NMe_2)	7.08—7.33 (m)		
(11)	4-$Me_2NC_6H_4$	4-MeC_6H_4	8.28	7.74 (d)	6.68 (d)	2.98 (s, NMe_2)	7.12 (s)	7.12 (s)	2.33 (s, Me)
(12) [k]	4-$Me_2NC_6H_4$	4-$MeOC_6H_4$	8.30	7.72 (d)	6.68 (d)	2.98 (s, NMe_2)	7.16 (d)	6.88 (d)	3.77 (s, OMe)
(13)	4-$MeOC_6H_4$	Ph	8.35 [l]	7.82 (d)	6.95 (d)	3.82 (s, OMe)	7.15—7.37 (m)		
(14)	4-$MeOC_6H_4$	4-MeC_6H_4	8.35	7.81 (d)	6.94 (d)	3.82 (s, OMe)	7.12 (s)	7.12 (s)	2.33 (s, Me)
(15)	4-$MeOC_6H_4$	4-$MeOC_6H_4$	8.37	7.80 (d)	6.93 (d)	3.82 (s, OMe)	7.17 (d)	6.89 (d)	3.78 (s, OMc
(16)	4-$MeOC_6H_4$	2,4,6-$Me_3C_6H_2$	8.09	7.82 (d)	6.95 (d)	8.32 (s, OMe)	2.10 (s, Mc)	6.87 (s)	2.27 (s, Me)
(17) [m]	3,4,5-$(MeO)_3C_6H_2$	4-MeC_6H_4	8.33	7.14	3.90, 3.92 (2s, 2OMe)		7.14 (s)	7.14 (s)	2.35 (Me)
(18) [n]	3,4,5-$(MeO)_3C_6H_2$	4-$MeOC_6H_4$	8.35	7.13 (s)	3.90, 3.92 (2s, 2OMe)		7.19 (d)	6.91 (d)	3.80 (s, MeO)
(19) [o]	3,4,5-$(MeO)_3C_6H_2$	2,4,6-$Me_3C_6H_2$	8.08	7.15 (s)	3.92, 3.93 (2s, 2 OMe)		2.10 (s, Me)	6.87 (s)	2.27 (s, Me)
(20)	2-HOC_6H_4	Ph	8.57 [p]	6.75—7.47 m					
(21)	2-HOC_6H_4	4-MeC_6H_4	8.57	6.73—7.47 (m)					
(22)	2-HOC_6H_4	4-$MeOC_6H_4$	8.55 [q]	6.73—7.50 (m)					
(23) [r]	2,4,6-$(MeO)_3C_6H_2$	4-MeC_6H_4	8.75	3.80 or 3.83 (s, OMe)	6.13 (s)	3.83 or 3.80 (s, OMe)	7.12 (s)	7.12 (s)	2.33 (s, Me)
(24) [s]	2,4,6-$(MeO)_3C_6H_2$	4-$MeOC_6H_4$	8.75	3.78 or 3.85 (s, OMe)	6.13 (s)	3.85 or 3.78 (s, MeO)	7.18 (d)	6.89 (d)	3.78 or 3.85 (s, MeO)
(25) [t]	2-BrC_6H_4	4-$MeOC_6H_4$	8.85	8.12—8.28 (m)	7.23—(7.67 (m)		7.26 (d)	6.92 (d)	3.82 (s, MeO)
(26)	2-$O_2NC_6H_4$	4-$MeOC_6H_4$	8.93	7.52—8.37 (m)			7.29 (d)	6.93 (d)	3.82 (s, MeO)
(27) [u]	2,6-$(O_2N)_2C_6H_3$	4-$MeOC_6H_4$	8.83		7.23 — 8.35 (m)		7.23 (d)	6.93 (d)	3.82 (s, MeO)
(28) [v]	2,4,6-$Me_3C_6H_2$	4-$MeOC_6H_4$	8.75	2.50 (s, Me)	6.88 (s)	2.28 (s, Me)	7.15 (d)	6.91 (d)	3.80 (s, MeO)

[a] Lit.,[b] 8.40. [b] K. Tabei and E. Saitou, *Bull. Chem. Soc. Japan*, 1969, **42**, 1440. [c] Lit.,[b] 8.39. [d] Lit.,[b] 8.45. [e] Lit.,[b] 8.54. [f] M.p. 135—136° (lit. 124.5°, F. Ullmann, *Ber.*, 1903, **36**, 1017). [g] M.p. 142—143°. [h] M.p. 126—127°. [i] M.p. 156—157°. [j] Lit.,[b] 8.29 [k] M.p. 145—146° (lit., 138—140°, F. Sachs and W. Lewin, *Ber.*, 1902, **35**, 3569). [l] Lit.,[b] 8.35. [m] M.p. 98—99°. [n] M.p. 109—110° [o] M.p. 111—112°. [p] Lit. 8.54; N. M. D. Brown and D. C. Nonhebel, *Tetrahedron*, 1968, **24**, 5655. [q] Lit.,[b] 8.60. [r] M.p. 96—97°. [s] M.p. 148—149°. [t] M.p. 73—74°. [u] M.p. 168—169°. [v] M.p. 68—69°.

haviour of the formyl proton in the parent aldehydes (Table 2), although differences in polarisation between C=O and C=N (estimated[13] bond moments 2.3 and 0.9 D respectively) are reflected in the greater deshielding of the formyl proton. In one case only, the direction of shift is different: in the aldehyde series *o*-hydroxy has a small shielding effect, whereas in the azomethine series it is deshielding, a difference which may be related to the strengths of the internal hydrogen bonds.

TABLE 2

Chemical shifts of formyl protons in aldehydes in CDCl$_3$

Compounds	δ
Benzaldehyde	9.97
p-Nitrobenzaldehyde	10.19
p-Dimethylaminobenzaldehyde	9.71
p-Anisaldehyde	9.89
3,4,5-Trimethoxybenzaldehyde	9.85
Salicylaldehyde	9.85
2,4,6-Trimethoxybenzaldehyde	10.34
o-Anisaldehyde	10.39[a,b]

[a] R. E. Klinck and J. B. Stothers, *Canad. J. Chem.*, 1962, **40**, 1071, 2329. [b] In CCl$_4$.

Klinck and Stothers[14] also observed deshielding of formyl protons in *ortho*-substituted aldehydes and attributed it to the steric effect of the substituent, resulting in twisting of the formyl group out of the plane of the aromatic ring with consequent reduction of the (shielding) conjugative effect of the ring on the electron density at the formyl carbon atom. As the inductive effect of the *ortho*-substituent is not affected by twisting, the net result depends on the nature of the substituent as well as its size, *e.g.* *o*-tolualdehyde (−0.22 p.p.m. from benzaldehyde) and *o*-nitrobenzaldehyde (−0.41 p.p.m. from benzaldehyde) (in CCl$_4$) where, although methyl and nitro are comparable in size, their inductive effects are in opposite directions. In mesitaldehyde (−0.53 p.p.m.) the second *o*-methyl group will increase the twist of the formyl group. The case of *o*-anisaldehyde (−0.43 p.p.m.) is less easily interpreted since methoxy is considerably smaller than nitro (if the methyl is turned away from the adjacent group) and yet has a comparable effect on the chemical shift of the proton; further, the introduction of a second methoxy group (as in 2,4,6-trimethoxybenzaldehyde, −0.45 p.p.m. from *p*-anisaldehyde) does not enhance this effect. While steric strain in mesitaldehyde can only be relieved by twisting of the formyl group, the strain in *o*-nitrobenzaldehyde may be reduced by twisting of either group or perhaps of both simultaneously. Similarly methoxy can rotate so that its C–O is not in the plane of the ring, and although its steric effect on CHO will not then be very large, it may well cause a downfield shift of the formyl proton because of the proximity of methoxy oxygen to this proton as long as the formyl group remains approximately in the plane of the ring [conformation (a) rather than (b)]. In this case the presence of a second *o*-methoxy-group would not augment the downfield shift because the formyl proton would only be close to *one* methoxy oxygen, not both. If, however, the formyl group were twisted through a large angle by *o*-methoxy it is hard to see why the second methoxy-group should not augment the effect of the first by increasing the angle of twist.

The energy barrier to rotation of the formyl group in aromatic aldehydes has been determined[15-17] by ^{1}H and ^{13}C n.m.r. studies at low temperatures. For benzaldehyde $\Delta G^{\ddagger}$ is 7.6 kcal mol^{-1} at −105° (in CHCl$_2$F + CCl$_2$F$_2$)[16] and for *p*-methoxybenzaldehyde the barrier is increased to *ca.* 9 kcal mol^{-1} at −90°. However, at least in deuteriotoluene, $\Delta G^{\ddagger}$ for *p*-methoxybenzaldehyde is temperature-dependent and increases to 12.4 at 27°. The energy barrier for rotation of the methoxy-group is smaller: the value for anisole determined by Owen and Hester[18] from i.r. and Raman spectra is 6.02 kcal mol^{-1}. It thus appears reasonable that rotation of methoxy should be preferred to rotation of formyl.

Bürgi and Dunitz[12] found that the aldehyde ring in azomethines is twisted out of the HC=N–C plane by only a small amount (10° in benzylideneaniline). This angle is insufficient to affect conjugation and, if it is maintained in the presence of small *o*-substituents, will leave the proton within the deshielding influence of the substituent, *e.g.* oxygen in methoxy. The barrier to rotation of the CH=N group has apparently not been determined but similarity between the two series of compounds suggests that here too [compounds (23) and (24)] rotation of methoxy is preferred. With the large spherically symmetrical substituents bromine and methyl, rotation of the CH=N group is to be expected and the observed shifts in compounds (25) and (28) can be correlated with the size and direction of the inductive effects of these substituents, although by analogy with mesitaldehyde a rather larger shift might have been expected for compound (28). One *o*-nitro group [compound (26)] is more deshielding than two [compound (27)]; again it seems likely that twisting of the nitro-group is important, and may happen preferentially as long as only one is present. The aldimine proton will then be strongly deshielded by its proximity to N and O. The steric effect of two *o*-nitro-groups is almost certainly large enough to cause twisting of the CH=N group as well (beyond the initial 10°) and the aldimine proton is thus further removed from the local deshielding influence. The balance of inductive effects, residual conjugative effects for medium angles of twist, and local deshielding effects (decreasing with increased twist of CH=N) can make the net effect on the aldimine proton very susceptible to small changes in angles.

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Rather surprisingly, *ortho*-substituents (Me, Cl) in the aniline ring of the azomethines have a shielding effect: this is *ca.* 0.10 for two chlorine atoms [compound (9) in comparison with (4)] and *ca.* 0.25 p.p.m. for two methyl groups [(7), (16), and (19) in comparison with (5), (14), and (17) respectively]. The aniline ring is already twisted out of planarity with N=CH–C by *ca.* 50° and the presence of two large *ortho*-substituents (which cannot make a contribution to relief of strain by their own rotation) will increase this angle to nearly 90°. A comparison of aliphatic and aromatic azomethines is of interest here. The purely aliphatic compounds, R^{1}CH$_a$=NR^2, have a chemical shift [19-21] of δ *ca.* 7.5—7.6 for H$_a$. When R^1 is replaced by Ar^1, as in Ar^{1}CH$_a$=NR^2, shielding of the proton by the aromatic ring causes a downfield shift [21] of −0.5 p.p.m. When R^2 is also replaced by Ar^2, giving Ar^{1}CH$_a$=NAr^2, a further downfield shift occurs (*ca.* 0.3 p.p.m.), although the twisting of the N–Ar^2 bond means that deshielding is not maximal. An increase in the angle of twist from *ca.* 50 to *ca.* 90°, however, brings the azomethine proton into a position where it is on the edge of the deshielding region of the aniline aromatic ring, so that while it is not experiencing actual shielding by the ring, it is not experiencing deshielding either (in terms of the calculated z, ρ co-ordinates for H, and Johnson and Bovey's diagram [22] of ' isoshielding ' lines in the neighbourhood of a benzene ring: for a dihedral angle of 50° H is in the region between −0.20 and −0.30; for an angle of 90°, it is marginally above the zero shielding line). The upfield shifts of +0.23 in going from (5) to (7), of +0.26 in going from (14) to (16), and of +0.25 p.p.m. in going from (17) to (19) are similar in magnitude to the shift in going from Ar^{1}CH=NAr^2 (with dihedral angle *ca.* 50°) to Ar^{1}CH=NR^2.

Only *E*-isomers of the azomethines have been considered since, in the benzene series, the *Z*-isomers have not been detected under ordinary conditions; [21,23] in *ortho*-disubstituted *C*-aryl-*N*-alkylaldimines however, Boyd *et al.*[24] have found that *E*-isomers equilibrate in solution to mixtures containing appreciable amounts of *Z*-isomers (21% in the most favourable case studied). *Z*-Isomers were detected [24] by the development of a second signal for NR^2; in the present work there was no evidence of a second signal for NAr^2.

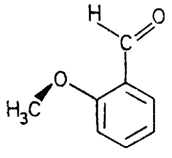
Aromatic Protons.—The approximate chemical shifts of the aromatic protons are given in Table 1. The spectra of the compounds containing 1,4-disubstituted aromatic rings have been treated as AB spectra rather than as AA'BB' spectra. It is clear that while CH=N has very little effect on the protons of the ring attached to nitrogen, it has a marked deshielding effect on the *ortho*-protons of the ring attached to carbon. Substituent effect on chemical shifts of aromatic protons are not strictly additive but, as shown in Supplementary Publication No. SUP 21570 (3 pp.) ,* there is sufficient consistency in the results for the azomethines with a single *para*-substituent in the aldehyde ring to give some confidence in the figures so determined. Protons *ortho* to the carbon of CH=N experience a downfield shift of *ca.* 0.60 p.p.m., relative to benzene. Protons *meta* to the carbon of CH=N experience a very slight downfield shift but it is not possible to quantify it from the evidence available.

Methyl Groups.—In the few mesityl compounds studied there is an interesting difference in the chemical shift of the *o*-methyl groups according to whether the mesityl group is attached to carbon or nitrogen of CH=N. Methyl groups *ortho* to carbon are deshielded (2.50 compared with 2.28 p.p.m. for *p*-methyl), whereas methyl groups *ortho* to nitrogen are shielded (2.10 compared with 2.28 p.p.m. for *p*-methyl). In the latter case, twisting of the ring through *ca.* 90° presumably brings the methyl protons within the shielding influence of the other ring.

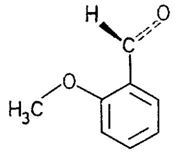
EXPERIMENTAL

Azomethines were prepared by standard methods, using a solvent and heat where necessary. Wherever possible they were crystallised from light petroleum since some of them underwent partial hydrolysis in hydroxylic solvents. Analytical data for new compounds are given in SUP 21570.

N.m.r. spectra were determined at 60 MHz for deuteriochloroform solutions with tetramethylsilane as internal standard on a Varian HA60 instrument.



(a)



(b)

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1974, Index issue. Items less than 10 pp. are supplied as full-size copies.

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