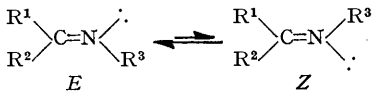
Equilibrium Distribution of *E–Z*-Ketimine Isomers

By **Johannes Bjørgo, Derek R. Boyd,*** and **Christopher G. Watson,** Department of Chemistry, Queen's University, Belfast BT9 5AG
W. Brian Jennings, Department of Chemistry, University of Birmingham, Birmingham B15 2TT

The ratio of *E–Z*-imine isomers at equilibrium is dependent on resonance stabilization, non-bonding interactions, substitution, and solvent. Stereochemical assignments are based upon i.r. and n.m.r. data.

ACYCLIC *N*-alkylimines in solution isomerize at ambient temperature ($\Delta G^{\ddagger}$ *ca.* 83—108 kJ mol^{-1}) by an inversion or rotation,[1-4] and in some cases *via* an imine–enamine tautomerism mechanism.[5] The equilibrium distribution has generally been interpreted in terms of non-bonded interactions and a preference for maximum resonance stabilization.[1-11] For simple aliphatic (trialkyl) imines these factors cause a higher proportion of the *E*-isomer



E *Z*

($R^1 > R^2$) to be present at equilibrium. It has previously been assumed that the bulkier group on the imine carbon atom prefers to be *trans* to the nitrogen substituent. In a preliminary report [12] we suggested that additional factors might contribute to the *E–Z* isomer ratio particularly in *C*-arylimines (R^1 = aryl, R^2 = R^3 = alkyl).

DISCUSSION

Steric and Resonance Factors.—The ratio of *E–Z*-imine isomers (1)—(6) (Table 1) illustrates the dominant influence of classical steric interactions between the *N*-alkyl group and the proximate *C*-alkyl or *C*-phenyl group. Thus the strong preference for the *E*-isomer in the aldimine (1) may be attributed to adverse repulsive interactions between the phenyl ring and the *N*-methyl group in the *Z*-configuration. Increasing the size of the *C*-alkyl substituent destabilizes the *E*-isomer and moves the equilibrium toward the *Z*-form (Table 1). Thus, a change of the *C*-alkyl group from n-propyl to isopropyl alters the equilibrium in favour of the *Z*-isomer. On this basis alone it would appear that the ' size ' of the phenyl group lies between n-propyl and isopropyl.

TABLE 1

Equilibrium distribution of *E–Z*-imine isomers at ambient temperature

Imine *p*-XC_6H_4·C(R^2)=NR^3	X	R^2	R^3	% *E* *
(1)	H	H	Me	100
(2)	H	Me	Me	93
(3)	H	Et	Me	74
(4)	H	Pr	Me	70
(5)	H	Pr^i	Me	5
(6)	H	Bu^t	Me	0
(7)	NO_2	Me	Me	97
(8)	NO_2	Me	Pr^i	95
(9)	NO_2	Me	Bu^t	98

* All imines were allowed to equilibrate at room temperature (*ca.* 25 °C) in $CDCl_3$ solution prior to analysis by multiple n.m.r. integration.

[1] C. G. McCarty in ' The Chemistry of the Carbon–Nitrogen Double Bond,' ed. S. Patai, Interscience, London, 1969, p. 363.
[2] J. M. Lehn, *Fortschr. Chem. Forsch.*, 1970, **15**, 311.
[3] H. O. Kalinowski and H. Kessler, *Topics Stereochem.*, 1973, **7**, 295.
[4] G. Wettermark, *Svensk. Kem. Tidskr.*, 1967, **79**, 249.
[5] W. B. Jennings and D. R. Boyd, *J. Amer. Chem. Soc.*, 1972, **94**, 7187.
[6] K. Tori, M. Ohtsuru, and T. Kubota, *Bull. Chem. Soc. Japan*, 1966, **39**, 1089.
[7] D. A. Nelson and R. L. Atkins, *Tetrahedron Letters*, 1967, 5197.
[8] D. Wurmb-Gerlich, F. Vogtle, A. Mannschreck, and H. A. Staab, *Annalen*, 1967, **708**, 36.
[9] E. Melendez, R. Perez Ossorio, and V. Sanchez del Olmo, *Anales. de Quim.*, 1970, **66**, 87.
[10] J. Hine and C. Y. Yeh, *J. Amer. Chem. Soc.*, 1967, **89**, 2669.
[11] G. J. Karabatsos and S. S. Lande, *Tetrahedron*, 1968, **24**, 3907.
[12] J. Bjørgo, D. R. Boyd, W. B. Jennings, and C. G. Watson, *Tetrahedron Letters*, 1972, 1747.

TABLE 2

Equilibrium distribution of *ortho*-substituted *E–Z*-imine isomers at ambient temperature

Imine Ar·C(R^2)=NR^3	Ar	R^2	R^3	% *E* *
(10)	2-Naphthyl	Me	Me	96
(11)	1-Naphthyl	Me	Me	22
(12)	1-Naphthyl	Me	Bz	23
(13)	1-Naphthyl	Me	Pr^i	24
(14)	1-Naphthyl	Me	Bu^t	36
(15)	1-Naphthyl	Et	Me	4
(16)	1-Naphthyl	Ph	Me	0
(17)	2-MeC_6H_4	Me	Me	24
(18)	2-MeC_6H_4	Ph	Me	0
(19)	2-MeOC_6H_4	Me	Me	42
(20)	2-$NO_2C_6H_4$	Me	Me	43
(21)	Mesityl	Me	Me	5
(22)	9-Anthryl	Me	Me	5

* See footnote to Table 1.

TABLE 3

Equilibrium distribution of *E–Z*-imine isomers at ambient temperature

Imine *p*-XC_6H_4·C(R)=NMe	X	R	% *E* *
(2)	H	Me	94
(3)	H	Et	72
(7)	NO_2	Me	97
(23)	NO_2	Et	81
(24)	MeO	Me	95
(25)	MeO	Et	76
(26)	Cl	Me	95
(27)	Cl	Et	75
(28)	Me	Ph	(53) †
(29)	MeO	Ph	64 (63) †
(30)	NMe_2	Ph	71 (70) †
(31)	Cl	Ph	60 (59) †
(32)	Br	Ph	64 (57) †
(33)	NO_2	Ph	68 (61) †
(34)	CF_3	Ph	(57) †

* See footnote to Table 1. † Analysed in C_6D_6 solution.

TABLE 4

Solvent effects on *E–Z*-isomer distribution

Solvent	% *E* isomer in imine * (11)	(30)	(33)
$CDCl_3$	22	71	68
CCl_4	18	68	71 †
C_6D_6	18	70	61
$C_6H_3Cl_3$	28	71	70
C_5D_5N	30	70	68
CD_3CN	33	73	61 †
$(CD_3)_2CO$	25	69	63 †
Bu^{t}OH	18	67 †	67 †

* Average values obtained by n.m.r. analysis in (0·5M) solution in Birmingham and Belfast. † Saturated solution (<0·5M).

It is noteworthy that in cyclohexane systems the phenyl group (*A* value 3·0) appears to be ' larger ' than the isopropyl group (*A* value 2·3).[13] However, the latter data reflect mainly [1,3] diaxial interactions whereas the imine ratios involve [1,2] eclipsing effects. Steric interactions between the *ortho*-hydrogen atoms of the phenyl ring and the *cis*-*N*-methyl group in the *Z*-isomer may be reduced by twisting of the aryl ring from the C=N molecular plane as depicted in (II-*Z*) (Figure 1). This effect will be opposed by the delocalization (resonance) energy which favours the coplanar conformation (I-*Z*). The net result will be a ground state conformation where the ring is slightly twisted out of the imine molecular plane. It has been reported that the *C*-phenyl ring in benzylideneaniline PhCH=NPh (in the crystalline state) is twisted from this plane by *ca.* 10° in the *E*-configuration.[14]

[13] Based on the ' best *A* values ' given by J. A. Hirsch, *Topics Stereochem.*, 1967, **1**, 199.

[14] H. B. Burgi and J. D. Dunitz, *Chem. Comm.*, 1969, 472.

TABLE 5

I.r. and n.m.r. data for imines

Imine	$\nu_{max.}$/cm^{-1} *E*	*Z*	Chemical shift (τ) of *N*-alkyl group: $CDCl_3$ *E*	*Z*	C_6D_6 *E*	*Z*
(1)	689		6·56			
(2)			6·67	6·95		
(3)			6·63	6·96		
(4)	688	696	6·60	6·95		
(5)			6·60	7·00		
(6)		701		7·17		
(7)			6·59	6·94		
(8)			8·77 [a]	8·92 [a]		
(9)			8·60 [b]	8·97 [b]		
(10)			6·64	6·94		
(11)			6·56	7·04		
(12)			5·23 [c]	5·80 [c]		
(13)			8·70 [a]	8·97 [a]		
(14)			8·51 [b]	8·98 [b]		
(15)			6·52	7·10		
(16)		694		6·87		
(17)			6·70	7·10		
(18)		692		6·83		
(19)			6·71	7·06		
(20)			6·67	7·10		
(21)			6·65	7·10		
(22)			6·34	7·09		
(23)			6·60	6·97		
(24)			6·70	6·90		
(25)			6·62	6·91		
(26)			6·65	6·94		
(27)			6·62	6·94		
(28)			6·77	6·74	6·79	6·75
(29)	702	692	6·83	6·74	6·80	6·74
(30)	701	694	6·85	6·68	6·75	6·60
(31)	701	693	6·77	6·76	6·88	6·92
(32)	701	693	6·78	6·76	6·88	6·93
(33)	702	692	6·71	6·79	6·87	7·01
(34)	701	692	6·68	6·73	6·87	6·98

[a] Pr^i doublet. [b] CBu^t singlet. [c] CH_2 singlet.

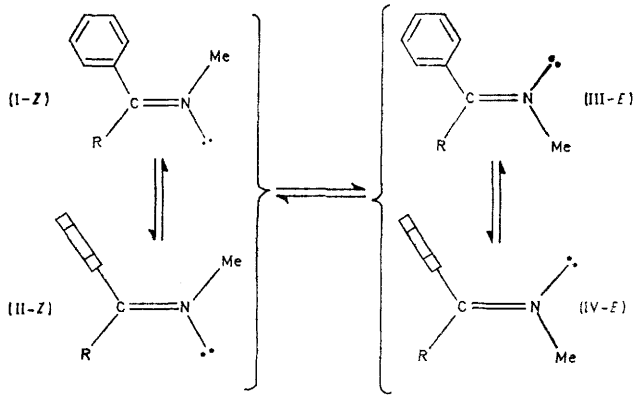


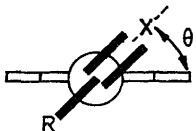
FIGURE 1 Conformational equilibria of *N*-methyl-imines

In contrast to the high sensitivity of the imine equilibrium position to *C*-alkyl group substitution, only minor changes were observed for a range of *N*-alkyl groups [Table 1, (7)—(9); Table 2, (11)—(14)].

ortho-*Substituent Effects.*—The introduction of an *ortho*-substituent on the *C*-aryl group results in a very marked change in isomeric preference toward the *Z*-form (Table 2). In energy terms the '*ortho*-effect' can be estimated (*ca.* 9·5 kJ mol^{-1} for an *o*-tolyl or a 1-naphthyl group and *ca.* 13·7 kJ mol^{-1} for a mesityl or 9-anthryl group) by comparing the isomer ratio of imines (11), (17), (21), and (22) with (2).

The *ortho*-effect may be explained to a large degree in conformational terms. Thus, steric interactions between the *ortho*-substituent and the *C*-alkyl or *N*-alkyl group (Figure 1) may force the aromatic ring further out of the C=N plane and toward the conformations (II-*Z*) and (IV-*E*). Support for this view may be derived from the τ values of the *N*-methyl signals. An inspection of Table 5 shows the *N*-methyl signals of the *Z*-isomer to be shifted upfield by *ortho*-substitution on the proximate aryl ring. For example, in the phenyl (2), *o*-tolyl (17), and mesityl (21) compounds τ (*Z*) values were 6·95, 7·10, and 7·10 respectively; in the 2-naphthyl (10), 1-naphthyl (11), and 9-anthryl (22) imines τ (*Z*) values were 6·94, 7·04, and 7·09 respectively. As anticipated the *N*-methyl signal positions of the *E*-isomers remain relatively unchanged on *ortho*-methyl substitution. A ring current effect in conformation (II-*Z*) can account for the *N*-methyl resonance upfield shift in *ortho*-substituted imines (Figure 1).

Estimates of the dihedral angle (θ) between the aryl and imino (A; X = NMe) planes may be obtained by



(A)

application of the equation of Johnson and Bovey.[15] Using standard bond lengths and the *X*-ray data reported for benzylideneaniline[14] the ring current effect was calculated to be −0·55 (downfield) and +0·30 p.p.m. (upfield) for the *N*-methyl group in conformations (I-*Z*) and (II-*Z*) respectively.[16] The resulting difference of 0·85 p.p.m. is much larger than the observed variation of *ca.* 0·15 p.p.m. between (17-*Z*) and (2-*Z*).* It would thus appear that the dihedral angle around the *C*-phenyl bond in the *Z*-isomer is only increased slightly (say 10 to 30°) on the introduction of an *ortho*-methyl group. This situation would obtain if the phenyl ring in (2-*Z*) were found in a conformation with a relatively large dihedral angle (θ) which could only increase slightly on *ortho*-substitution. Attempts to calculate the angle θ in the *E*-isomer by consideration of the *C*-methyl protons were thwarted by the estimated ring current effect being of similar magnitude and direction in conformations (III-*E*) and (IV-*E*). The preferred conformation of the aryl ring in *E*-imines should be very similar to that found in the corresponding ketones (X = O). Dihedral angles for the ketones corresponding to imines (17) and (19)—(21) have been estimated at 28, 35, 24, and 51° respectively [compared to the ketone analogous to (2) where θ is considered as zero] from consideration of the aryl proton [17] and carbon-13 [18] chemical shifts.

It is thus clear that the increase in dihedral angle associated with *ortho*-substitution will tend to reduce the adverse steric interactions with the proximate *N*-methyl group in the *Z*-isomer. A possible explanation of the preference toward the *Z*-isomer on *ortho*-substitution may lie in the assumption that the 'size' of, for example, the mesityl and 9-anthryl groups in the orthogonal conformations [(II-*Z*) and (IV-*E*)] is considerably smaller than that of the *C*-methyl group. Anderson and Pearson [19] have recently suggested that in the eclipsed conformation of some ethane systems the 'size' of a phenyl group is similar to or perhaps slightly less than a methyl group. By contrast, however, the *ortho*-substituted ring of imines (11)—(22) prefer a conformation with a smaller dihedral angle in the *E*-isomer (relative to *Z*-isomer); thus the delocalization energy will tend to stabilize the *E*-isomeric form.

A close examination of Courtauld (Figure 2a) and Catalin (Figure 2b) space filling models does not support the view that either an aryl (*e.g.* mesityl or 9-anthryl) group is significantly smaller than a methyl group in substituted ketimines. There appears to be virtually no difference between the methyl and aryl groups even in the extreme cases shown (θ = 90°) which might not in practice be the preferred conformation.

In view of this rather unconvincing steric explanation for the *Z*-preference on *ortho*-substitution, additional factors should be considered. A preliminary report suggested that the *E*-isomer might be destabilized by a repulsive interaction between the nitrogen lone pair and the aromatic π-electrons in conformation (IV-*E*).[12] Support for this hypothesis may be obtained from a recent paper by Baker and Dyall [20] on hydrogen bonding in a phenyl-substituted *endo*-norbornanol. An n–π repulsive effect between the aryl ring and the proximate

* The estimation of the ring current effect is very approximate; the tables of C. W. Haigh and R. B. Mallion, *Org. Magnetic Resonance*, 1972, **4**, 203, suggest that the difference between (I-*Z*) and (II-*Z*) may be only *ca.* 0·4 p.p.m. Additionally, the imino and methyl substituents may introduce perturbations.

[15] C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, 1958, **29**, 1012.

[16] The average position of the methyl hydrogens was taken as the centre of a circle passing through the three nucleii. The ring current effect was determined from the Tables in Appendix B of J. W. Emsley, J. Feeny, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy,' Pergamon, London, 1965, vol. 1.

[17] G. Montaudo, P. Finocchiaro, and P. Maravigna, *J. Amer. Chem. Soc.*, 1971, **93**, 4214.

[18] K. S. Dhami and J. B. Stothers, *Tetrahedron Letters*, 1964, 631; *Canad. J. Chem.*, 1965, **43**, 479.

[19] J. E. Anderson and H. Pearson, *Chem. Comm.*, 1971, 871.

[20] R. Baker and L. K. Dyall, *J. Chem. Soc.* (*B*), 1971, 1952.

oxygen lone pairs was suggested by the conformational preference (*ca.* 5·0 kJ mol^{-1}) for the hydrogen bonded form.

Intermolecular repulsive interactions between π-systems and heteroatom lone pairs have been proposed

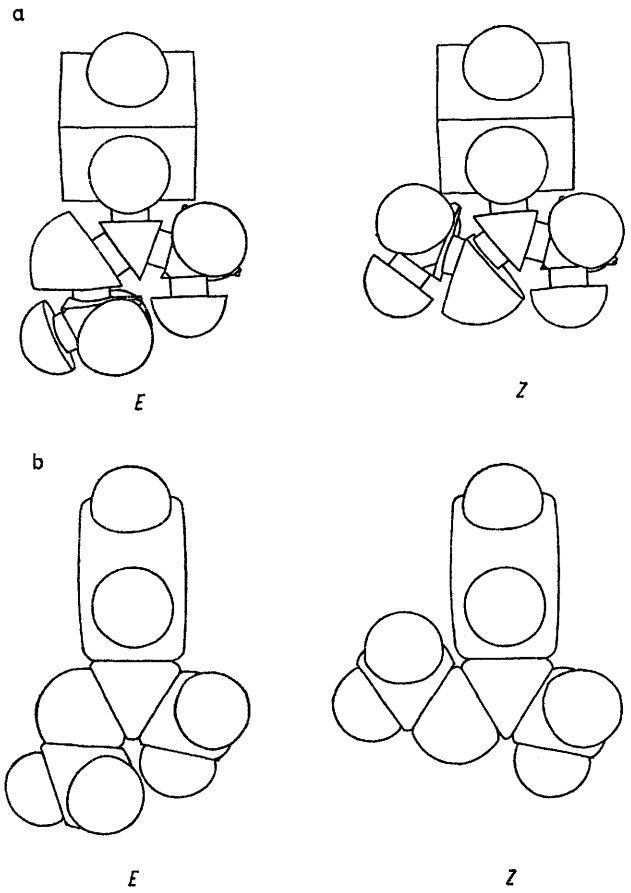
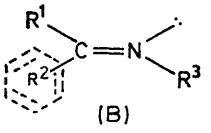


FIGURE 2 Space filling models of imines

to account for selective shifts of protons in aromatic solvents. Thus the solute–solvent collision complex (B) suggested for imines in benzene solution leads to preferential shielding of the protons in group R^2, which will minimize intermolecular *n*–π repulsion between the benzene π-cloud and the nitrogen lone pair.[6,11]



(B)

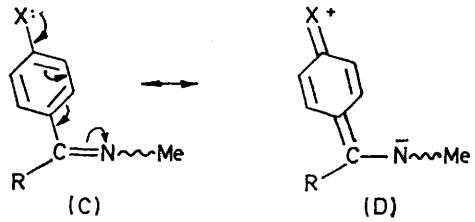
Interorbital lone pair repulsion effects have been considered to be important factors in the observation of the *anti*-form exclusively in methyl imidates [21] and in a preference for the *anti*-form of large (*n* = 11—13) methyl thioimidate rings [22] at equilibrium. Newkome and Bhacca [23] have reported an *ortho*-effect on the *Z*–*E*-isomer distribution in acetophenone *NN*-dimethylhydrazones. The equilibrium position was observed to change from 100% *E*-isomer (*o*-H substituent) to 53% *E* (*o*-Me substituent). In this example there was no marked preference for the *Z*-configuration as observed in the corresponding *o*-methylacetophenone imine (17). The effect of *ortho*-substitution in diaryl oximes has also been considered in terms of aryl conformations.[24]

While there would thus appear to be tentative evidence for an *n*–π repulsive interaction in other systems the evidence for an analogous effect in imines is similarly difficult to provide in an unequivocal or a quantitative manner.

para-*Substituent Effects*.—A series of *para*-substituted alkyl-aryl and diaryl imines were synthesized and analysed by n.m.r. (Table 3). While the *para*-substituent effect in acetophenone *N*-methylimines was barely outside experimental error (3—7% *Z*), a larger and consistent trend was observable in propiophenone *N*-methylimines (19—28% *Z*) and particularly in benzophenone *N*-methylimines (30—47% *Z*).

The lack of correlation between the percentage *Z*-isomer at equilibrium and the Hammett σ value of the *para*-substituent was rather unexpected. Furthermore, the consistent decrease in the *Z*-isomeric preference on *para*-substitution also provided a surprising contrast with the increase in *Z*-imine on *ortho*-substitution.

An electron-donating group on the *para*-position would tend to stabilize the coplanar conformation by increasing the delocalization energy [(C) ⟷ (D)]. This effect would increase the barrier to rotation around the *C*-aryl bond and move the equilibrium toward the *E*-isomer. Thus in terms of both resonance energy and



(C) (D)

steric effects electron-donating substituents should favour the *E*-imine in the order $NMe_2 > OMe > H$ (*cf.* the analogous *para*-substituted ketones [25]). On this basis electron-withdrawing substituents should have an opposite effect, *i.e.* destabilize the *E*-isomer; this reverse trend was not however observed in practice.

The more complex behaviour on *para*-substitution may also be investigated by reference to the τ values of the *N*-methyl group (Table 5).

The introduction of a *para*-nitro-group does not significantly alter the position of the *N*-methyl signal ($\Delta\tau < 0{\cdot}02$ p.p.m.) in the *Z*-isomers of acetophenone,

[21] R. M. Moriarty, C. L. Yeh, K. C. Ramey, and P. W. Whitehurst, *J. Amer. Chem. Soc.*, 1970, **92**, 6360.
[22] E. L. Yeh, R. M. Moriarty, C. L. Yeh, and K. C. Ramey, *Tetrahedron Letters*, 1972, 2655.
[23] G. R. Newkome and N. S. Bhacca, *J. Org. Chem.*, 1971, **36**, 1719.
[24] P. A. S. Smith and E. P. Antoniades, *Tetrahedron*, 1960, **9**, 210.
[25] H. Kessler, *Angew Chem. Internat. Edn.*, 1970, **9**, 219.

propiophenone, and benzophenone derived imines. In view of the previous estimation of a chemical shift of *ca.* 0·85 p.p.m. being associated with a change of 90° in θ, it appears that the electron-withdrawing nitro-substituent does not significantly alter the aryl ring conformation in the *Z*-isomer. The larger downfield shift (*ca.* 0·08 p.p.m.) in (33-*E*) (Table 5) may result from an increase in coplanarity of the unsubstituted ring thereby compensating for the diminished conjugation of the *p*-nitrophenyl ring. The strongly electron-donating dimethylamino-substituent appears to have a significant effect on both the *Z*-isomer (*ca.* 0·12 p.p.m. downfield) and the *E*-isomer (*ca.* 0·05 p.p.m. upfield). This result would be consistent with the dimethylaminophenyl group preferentially adopting a more coplanar conformation (θ ⟶ 0°).

The interpretation of isomer ratios in Table 3 in terms of simple dipolar interactions would be unsatisfactory in view of the consistent increase in *E*-isomer at equilibrium regardless of the direction of the resultant dipole after *para*-substitution.

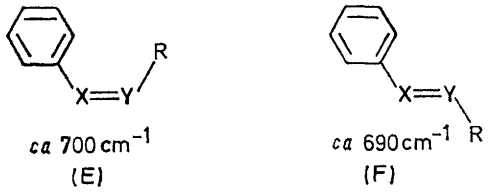
Among possible additional factors which may lead to destabilization of the *Z*-configuration in the presence of electron-withdrawing *para*-substituents [*e.g.* (33)] should be included *n*–π repulsive interactions. Repulsion between the nitrogen lone pair and the electron deficient *p*-nitrophenyl ring could be less than that found with the unsubstituted phenyl ring, thus favouring the *E*-configuration. The *n*–π effect would operate in the opposite direction for electron-donating substituents, but it could be counter-balanced by the resonance energy and strong preference toward coplanarity of the substituted ring. Nevertheless, it is possible that other more subtle influences are involved in the *para*-effect and it is not considered prudent to draw any firm conclusions on the basis of the presently available data. While the results in Tables 1—3 demonstrate clearly the major role of classical steric and resonance effects in the imine equilibrium distribution, the increase in *E*-isomer associated with polar *para*- (and probably *ortho*-) group substitution, allied to the increase in *Z*-isomer associated with both polar and non-polar *ortho*-group substitution illustrates the presence of additional parameters which should be considered in the determination of the equilibrium isomeric distribution of *C*-aryl substituted imines.

Solvent Effects.—The *E*–*Z* ratio in dialkyl ketimines has been reported to be identical in CCl_4 and C_6D_6 solutions;[11] however, preliminary results from these laboratories on *C*-aryl aldimines suggested the presence of a small solvent effect.[26]

Representative unsubstituted alkyl aryl (11) and polar substituted diaryl (30) and (33) imines were allowed to equilibrate in a range of solvents (Table 4). The equilibrium positions shown in Table 4 appear to be more dependent on the nature of the imine substituents than on the solvent used. The small range of values found for the diaryl imine (30) provides rather weak evidence for preferential solvation; however, the range shown by imines (33) (*ca.* 10%) and (11) (*ca.* 15%) clearly demonstrates that solvent selection may be a relatively important factor in the equilibrium position of *E*–*Z*-ketimine isomers.

Stereochemical Assignments.—The stereochemistry of the alkyl aryl imines (1)—(15), (17), and (19)—(27) was determined by n.m.r. analysis. The τ values (Table 5) for the *N*-alkyl groups were entirely consistent with structures previously deduced from dipole moment or *X*-ray,[1] and n.m.r. data (nuclear Overhauser effects,[27] solvent shift,[11] and HCCNCH,[11] ^{15}NCH,[28] and ^{13}CH coupling constants [28]). The higher τ values for *N*-alkyl groups in the *Z*-configuration result from the shielding effect of the aryl ring. The increasing preference for the aryl ring to adopt conformation (II-*Z*) (Figure 1) is illustrated by the alteration in τ values in the sequence (1)—(6).

The assignment of stereochemistry to the diaryl ketimines (16), (18), and (28)—(34) is more difficult and depends largely on the i.r. method used by Curtin and Hausser [29] for imines (31) and (33). A sharp absorption singlet (previously attributed to the C–H out-of-plane deformation vibration of monosubstituted aryl rings) was found to occur at *ca.* 700 cm^{-1} when the phenyl ring was *cis* to the group R [(E)] and at *ca.* 690 cm^{-1} in a



trans-relationship (F) for olefins (X = Y = C) and azo-compounds (X = Y = N) of known configuration. Application of this technique to the imines (1), (4), and (6) of known configuration (X = C, Y = N) supports the previously reported [29] extension of this procedure to diaryl imines. While imines (29), (30), and (33) crystallize out exclusively in the *E*-form, (16), (31), (32), and (34) appear as homogeneous crystals of the *Z*-configuration. Observation by i.r. and n.m.r. of the relevant absorption peak (Table 5) at ambient temperature showed a decrease in intensity with time and the gradual formation of a new peak consistent with a ready stereomutation process. At equilibrium in solution the *E*-form appeared to be favoured in imines (29)—(34), whereas imines (16) and (18) remained entirely in the *Z*-isomeric form. The liquid imine (28) was found to be present as an isomeric mixture with a slight bias toward the *E*-isomer on the basis of n.m.r. analysis.

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TABLE 6

Physical and microanalytical data for imines

Imine	B.p. (°C) [*p*/mmHg]	M.p. (°C)	Found (%) C	H	N	Formula	Required (%) C	H	N
(1)	74 [16] [a]								
(2)	96—98 [13] [b]								
(3)	43—46 [0·05] [c]								
(4)	32—34 [0·15]		81·4	9·4	8·45	$C_{11}H_{15}N$	81·9	9·4	8·7
(5)	102—104 [20]		81·6	9·1	8·9	$C_{11}H_{15}N$	81·9	9·4	8·7
(6)	92—94 [8]		82·4	9·8		$C_{12}H_{17}N$	82·3	9·45	
(7)		71—73	60·5	5·5	15·45	$C_9H_{10}N_2O_2$	60·7	5·6	15·7
(8)	95 [0·05]		64·0	6·8	13·5	$C_{11}H_{14}N_2O_2$	64·1	6·8	13·6
(9)	110 [0·1]		65·2	7·3	12·7	$C_{12}H_{16}N_2O_2$	64·5	7·3	12·7
(10)		32—33	85·0	7·0	7·4	$C_{13}H_{13}N$	85·25	7·1	7·65
(11)		68—69	85·3	7·1	7·6	$C_{13}H_{13}N$	82·25	7·1	7·65
(12)	157 [0·02]		88·25	6·55	5·4	$C_{19}H_{17}N$	88·0	6·6	5·4
(13)		78	85·45	6·7	8·2	$C_{15}H_{17}N$	85·3	6·6	8·1
(14)	77—80 [0·06]		85·4	8·3		$C_{16}H_{19}N$	85·3	8·5	
(15)		52—54	85·5	7·8	7·1	$C_{14}H_{15}N$	84·2	7·7	7·1
(16)		59—61	88·0	6·1	5·65	$C_{18}H_{15}N$	88·1	6·2	5·7
(17)	39 [0·5]		81·9	8·6	9·3	$C_{10}H_{13}N$	81·6	8·9	9·5
(18)	99—100 [0·3]		86·2	7·3	6·5	$C_{15}H_{15}N$	86·1	7·2	6·7
(19)	49—50 [0·1]		73·3	8·3	8·7	$C_{10}H_{13}NO$	73·6	8·0	8·6
(20)	78 [0·1]		60·4	5·7	15·5	$C_9H_{10}NO_2$	60·7	5·7	15·7
(21)	64—66 [0·1]		82·0	10·0	7·7	$C_{12}H_{17}N$	82·2	9·8	8·0
(22)		130—131	87·4	6·6	5·9	$C_{17}H_{15}N$	87·5	6·4	6·0
(23)		46—48	62·5	6·3	14·7	$C_{10}H_{12}N_2O_2$	62·5	6·3	14·6
(24)	110—112 [0·3]		73·3	7·8	8·8	$C_{10}H_{13}NO$	73·6	8·0	8·6
(25)	86 [0·1]		74·55	8·6	7·8	$C_{11}H_{15}NO$	74·5	8·5	7·9
(26)		60	64·5	6·1	8·4	$C_9H_{10}ClN$	64·5	6·0	8·4
(27)	69—71 [0·07]		66·2	6·6	7·8	$C_{10}H_{12}ClN$	66·1	6·7	7·7
(28)	122—124 [0·05]		86·0	7·0	6·5	$C_{15}H_{15}N$	86·1	7·2	6·7
(29)		52—54	79·7	6·9	6·2	$C_{15}H_{15}NO$	80·0	6·7	6·2
(20)		94—96	80·8	7·6	11·5	$C_{16}H_{18}N_2$	80·6	7·6	11·75
(31)		80—90 [d]							
(32)		89—90	61·3	4·5	5·1	$C_{14}H_{12}BrN$	61·3	4·4	5·1
(33)		125—126 [d]							
(34)		99—100	68·3	4·6	5·2	$C_{15}H_{12}F_3N$	68·4	4·6	5·3

[a] Lit.,[31] b.p. 92—93° at 34 mmHg. [b] Lit.,[32] b.p. 57—58° at 0·65 mmHg. [c] Lit.,[33] b.p. 102° at 20 mmHg. [d] Lit.,[29] m.p. 90—91°. [e] Lit.,[29] m.p. 126—127°.

EXPERIMENTAL

All imines were synthesized from the corresponding aldehyde or ketone and primary amine by standard literature methods.[30] Physical properties and microanalytical data are presented in Table 6.

I.r. spectra were obtained using a Spectromajor S-600 (Grubb–Parsons) instrument and the imines (5–10 mg ml^{-1}) dissolved in cyclohexane (Hopkins and Williams spectroscopic grade).

N.m.r. spectra were obtained using Varian XL-100 and Perkin-Elmer R-12 instruments at Birmingham and HA-100 and A-60 instruments at Belfast after the imines (0·5M) had been dissolved in the appropriate solvents. All imines were allowed to equilibrate at room temperature prior to n.m.r. analysis. Imine ratios were estimated to have an experimental error of ±2%, after duplicate experiments and multiple integrations. Figures 2a and 2b are exact copies taken from photographs of Courtauld and Catalin space-filling models of the imines.

We thank Messrs. W. J. Swindall and H. B. McKnight for microanalytical data, Dr. L. Waring and Mr. I. Jack for HA-100 n.m.r. spectra, and the Queen's University of Belfast for demonstratorships to J. B. and C. G. W.

[3/2141 *Received*, 19*th October*, 1973]

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