Thermal Equilibration of *Z*- and *E*-Isomers of 5-Arylmethylenehydantoins. Evidence for Non-bonded Aromatic π··· Methyl Attractions

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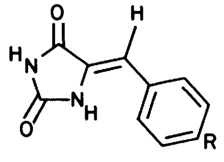
Standard free energy differences between the *Z*- and *E*-isomers of 14 5-arylmethylenehydantoins have been estimated by thermal equilibration in dimethyl sulphoxide. The *Z*-configuration is more stable for the *N*-unsubstituted compounds while the *E*-configuration is preferred for those *N*-1 methyl derivatives with only *para*-substituents in the aryl group. The ΔG° values vary with the nature of the *para*-substituents. For those *N*-1 methyl derivatives with two *ortho*-substituents in the aryl group, the configurational preference is dependent on the electronic effects of these aryl substituents, suggesting the presence of non-bonded aromatic π··· Me interactions. The factors influencing the relative stabilities of *Z*- and *E*-isomers are discussed.

The preparations and configuration assignments of some 5-arylmethylenehydantoins (**1**)—(**10**) have been reported.[1] Although geometrical isomerism is expected from restricted rotation about the exocyclic C=C double bound, all the *N*-unsubstituted compounds (**1**)—(**5**) were obtained almost exclusively in the *Z* form. In large-scale preparations of 5-benzylidenehydantoin (**1**), a very small yield of the *E* form was also isolated.[2] In contrast, from similar preparations of the N-1 methyl-substituted analogues (**6**)—(**10**), both *Z*- and *E*-isomers were readily isolable in various proportions.

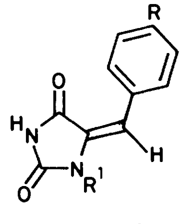
Examination of molecular models shows that in the *Z*-configuration of compounds (**1**)—(**5**), it is possible for the hydantoin and the benzene rings to be co-planar, with the N-1–H and the aryl *ortho*-H at almost touching distance whereas a similar co-planar conformation of the *E*-configuration will encounter severe steric repulsion between the aryl *ortho*-H and the C-4 carbonyl oxygen which possesses lone-pair orbitals. Rotating the aryl group slightly out of co-planarity can relieve this steric strain but will at the same time weaken the resonance interaction between the two rings. *X*-Ray crystallography has not only confirmed the configuration of (*Z*)-(**2**) which was previously assigned based on spectroscopic properties[1] but also revealed a virtually flat molecule with only a small angle of twist of 5.4°.[3]

Introduction of a bulky methyl substituent at the N-1 position in compounds (**6**)—(**10**) makes co-planarity in the *Z*-configuration impossible but it should have less effect on the steric crowding in the *E*-configuration. *X*-Ray analysis[4,5] confirms that the molecule of (*Z*)-(**6**) has a distinctly twisted conformation with a dihedral angle of 45.9° between the planes of the two rings. In contrast, the molecule of (*E*)-(**6**) remains nearly co-planar with an angle of twist of 5.7°.

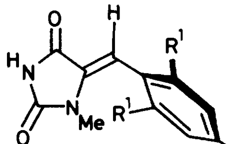
Hence, for the *N*-unsubstituted compounds (**1**)—(**5**) the predominance of the *Z*-isomers may be attributed mainly to the greater steric repulsion in the *E*-configuration. For the 1-methyl-substituted compounds (**6**)—(**10**), the loss of resonance stabilization in the *Z*-isomers that results from twisting of the aryl group substantially out-of-plane could be the most important factor contributing to the preference of these compounds for the *E*-configuration for which conjugation energy remains appreciable.



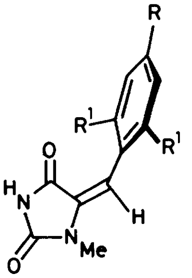
(*Z*)-(**1**) R = H
(*Z*)-(**2**) R = OMe
(*Z*)-(**3**) R = Me
(*Z*)-(**4**) R = Cl
(*Z*)-(**5**) R = CN



(*E*)-(**1**) R = R^1 = H
(*E*)-(**6**) R^1 = Me, R = H
(*E*)-(**7**) R^1 = Me, R = OMe
(*E*)-(**8**) R^1 = Me, R = Me
(*E*)-(**9**) R^1 = Me, R = Cl
(*E*)-(**10**) R^1 = Me, R = CN



(*Z*)-(**6**) R = H, R^1 = H
(*Z*)'-(**7**) R = OMe, R^1 = H
(*Z*)-(**8**) R = Me, R^1 = H
(*Z*)-(**9**) R = Cl, R^1 = H
(*Z*)-(**10**) R = CN, R^1 = H
(*Z*)-(**11**) R = R^1 = Me
(*Z*)-(**12**) R = R^1 = OMe
(*Z*)-(**13**) R = H, R^1 = Cl
(*Z*)-(**14**) R = H, R^1 = F



(*E*)-(**11**) R = R^1 = Me
(*E*)-(**12**) R = R^1 = OMe
(*E*)-(**13**) R = H, R^1 = Cl
(*E*)-(**14**) R = H, R^1 = F

In order to study the relative stabilities of these *Z*/*E* isomers, their standard free energy differences were determined by thermal equilibration. In addition, four other 5-arylmethylene-1-methylhydantoins (**11**)—(**14**) have been synthesized, each with both *ortho*-hydrogens replaced by bulkier substituents which effectively prevent co-planarity and therefore disrupt conjugation in both configurations, so as to probe the presence of any other factors determining the relative stabilities of their *Z*/*E* isomers.

Table 1. Thermal equilibration of (*Z*)- and (*E*)-5-arylmethylenehydantoins in dimethyl sulphoxide at 433 K

Equilibrium constant $K = [Z]/[E]$ and standard free energy difference $\Delta G^\circ = -RT\ln K$

Compd.	Z(%)	E(%)	K	ΔG°(kJ mol^{-1})
(1)	95.5	4.5	21.2	−11.0
(2)	95.9	4.1	23.4	−11.4
(3)	94.5	5.5	17.2	−10.2
(4)	93.6	6.4	14.6	−9.7
(5)	93.5	6.5	14.4	−9.6
(6)	32.6	67.4	0.48	2.6
(7)	30.6	69.4	0.44	3.0
(8)	33.4	66.6	0.50	2.5
(9)	28.0	72.0	0.39	3.4
(10)	23.9	76.1	0.31	4.2
(11)	75.2	24.8	3.03	−4.0
(12)	71.1	28.9	2.46	−3.2
(13)	46.6	53.4	0.87	0.5
(14)	39.8	60.2	0.66	1.5

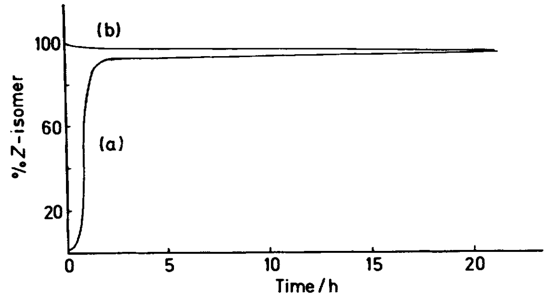


Figure 1. Thermal equilibration of *Z*- and *E*-isomer of compound (**1**) at 433 K (a) starting from *E*-isomer; (b) starting from *Z*-isomer

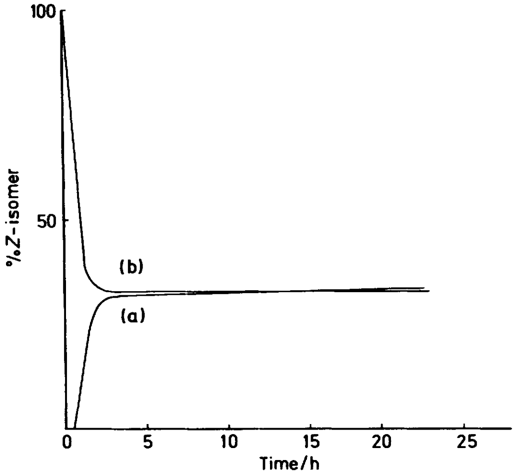


Figure 2. Thermal equilibration of *Z*- and *E*-isomer of compound (**6**) at 433 K (a) starting from *E*-isomer; (b) starting from *Z*-isomer

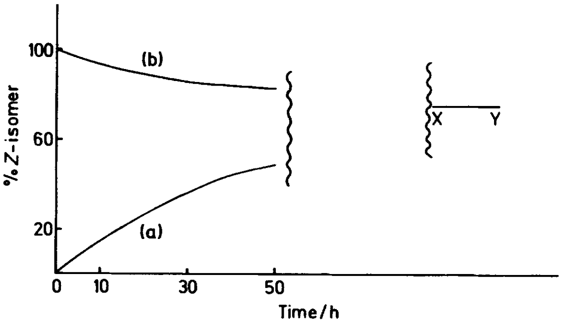
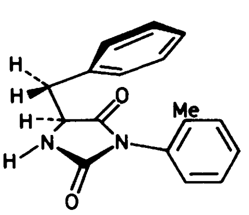


Figure 3. Thermal equilibration of *Z*- and *E*-isomer of compound (**11**) at 433 K (a) starting from *E*-isomer; (b) starting from *Z*-isomer. X-Y are points obtained by equilibrating mixtures near the equilibrium position

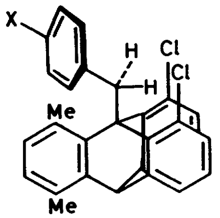
Results and Discussion

Although the C=C double bond normally has high configurational stability, isomerization can be brought about by photochemical, thermal, or chemical methods. The 5-arylmethylenehydantoins under study have been found to undergo photoisomerization readily. Thermal isomerizations of compounds (**1**)—(**14**) were conducted in dimethyl sulphoxide solutions and monitored by ^{1}H n.m.r. spectroscopy. Since the isomers of each compound give rise to different sets of signals, their relative concentrations are conveniently determined by integration of the areas of appropriate peaks, particularly the well separated signals of the respective vinyl protons and/or the N-1 methyl protons in the case of the 1-methyl-substituted compounds. Dimethyl sulphoxide was chosen as the solvent because of its usable temperature range and solubilities of the compounds studied. With compounds (**1**) and (**6**)—(**14**), equilibrium was attained starting from either of the pure isomers, whereas with compounds (**2**)—(**5**) only the *Z*-isomers were heated until a steady state was reached. However, on prolonged heating some decomposition was observed. This, together with the low percentage of *E*-isomer at equilibrium, limits the accuracy of the equilibrium constants for compounds (**1**)—(**5**). For compounds (**6**)—(**14**), the period of heating and the extent of decomposition was reduced by allowing equilibration of a mixture of *Z*- and *E*-isomers of composition approximate to the equilibrium point as determined earlier from heating the separate isomers. In these experiments, the relatively high temperature of 433 K was chosen to achieve conveniently followed rates of isomerization and reproducible results. At lower temperatures, the slow rates necessitate prolonged periods of heating and make determination of equilibrium positions less certain while higher temperatures cannot be used because of the boiling point of the solvent. The equilibrium constants and the standard free energy changes ΔG° are given in Table 1.

The three groups of compounds (**1**)—(**5**), (**6**)—(**10**), and (**11**)—(**14**) present somewhat different patterns of thermal isomerization as exemplified by those of (**1**), (**6**), and (**11**) in Figures 1, 2, and 3, respectively. The superior stability of the *Z*-isomers of the *N*-unsubstituted compounds is evidenced by the very slow change of (*Z*)-(**1**) compared with the rapid isomerization of (*E*)-(**1**) and by the very high *Z*/*E* ratio at equilibrium. By contrast, (*Z*)-(**6**) isomerizes slightly faster than (*E*)-(**6**) and equilibrium favours the *E*-isomer. The main reason for this observed reversal of configurational preference of compounds (**6**)—(**10**) is probably not the enhanced stability of their *E*-isomers but relative destabilization of their *Z*-isomers. That is to say, the stabilities of (*E*)-(**6**) and (*E*)-(**1**) are probably not appreciably different but (*Z*)-(**6**) is less stable than (*Z*)-(**1**). That the stability differences between the isomers are greater in the series (**1**)—(**5**) than in the series (**6**)—(**10**) is reflected by the much larger negative ΔG° values for the former and smaller positive ΔG° values for the latter compounds. Both (*Z*)-(**11**) and (*E*)-(**11**) undergo isomerization very slowly with the *E*-isomer isomerizing slightly faster than the *Z*-isomer. Considerable side-reactions occur on prolonged heating so that a reasonably good equilibrium value can only be obtained by heating mixtures of the two isomers. The very much slower rates of isomerization of compounds (**11**)—(**14**), each with two bulky *ortho* substituents, are probably due to the high energy barrier to rotation.



(A)

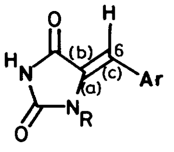


(B) X = NMe_2, H, or NO_2

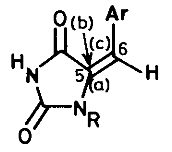
Comparison of the equilibrium constants among compounds (**6**)—(**10**) reveals differences attributable to electronic effects of the *para* substituents in the benzene ring. The equilibrium *Z*/*E* ratio is higher when the substituent is electron-releasing and smaller when it is electron-withdrawing, suggesting the possible existence of a stabilizing mechanism that is favoured by increased electron density in the benzene ring. This could be similar to the weak aromatic $\pi \cdots$ H–C attractions which have been studied both experimentally and by theoretical calculations.[6–9] Manifestation of aromatic $\pi \cdots$ Me interaction in molecules of suitable geometry has been elegantly demonstrated in 5-benzyl-3-tolylhydantoin (**A**)[10–12] and in some 9-(4-substituted benzyl)-8,13-dichloro-9,10-dihydro-1,4-dimethyl-9,10-*o*-benzenoanthracenes (**B**).[13] The former compound (**A**) has been shown to prefer the more sterically crowded conformation with the benzene ring very close to the methyl of the tolyl group. Among the latter series of compounds (**B**), the conformation with the ring of the benzyl group close to the 1-methyl group is increasingly preferred when the X-substituent is electron-releasing. In the *Z*-configuration of (**6**)—(**10**), the N-1–Me is positioned over the plane of the aryl ring and therefore favourably oriented for operation of such non-bonded attractions. Moreover, compared with the *C*-methyl groups in question in compounds (**A**) and (**B**) the 1-methyl group in (**6**)—(**10**), being attached to an amide nitrogen, is more acidic and may be expected to interact more strongly with the aromatic π electrons.

Compounds (**11**)—(**14**) provide further corroborative evidence for the presence of these non-bonded attractions. The two *ortho* substituents in each compound effectively restrict rotation of the aryl group and prevent co-planarity in both *Z*- and *E*-configurations. *X*-Ray crystallography confirms these non-planar structures with dihedral angles of 84.2 and 57.1° for the *Z*- and *E*-isomer of compound (**11**), respectively.[14] Hence, the resonance effect which contributes to the greater stability of the *E*- *versus* the *Z*-isomers of compounds (**6**)—(**10**) is no longer applicable to compounds (**11**)—(**14**). One remaining important factor which influences the relative stabilities of the isomers of (**11**)—(**14**) could be the difference in the interactions of the aromatic π-electrons which are attractive towards the N-1–Me protons in the *Z*-isomers but repulsive towards the lone pairs on the C-4 carbonyl oxygen in the *E*-isomers. The extent of these interactions will in turn be affected by the electronic nature of the aryl substituents. The electron-releasing 2,4,6-trimethyl or -trimethoxy groups in compounds (**11**) and (**12**) should enhance any aromatic $\pi \cdots$ Me attraction and consequently favour the *Z*-configuration. The electron-withdrawing 2,6-dichloro- or -difluoro substituents in compounds (**13**) and (**14**) should have the opposite effect. In agreement with this, it is observed that, at thermal equilibrium, *Z* is the preferred isomer for compounds (**11**) and (**12**) while *E* is preferred for compounds (**13**), (**14**) with corresponding reversal of the sign of ΔG°. The smaller magnitudes of their ΔG° values reflect the more delicately balanced stabilizing and destabilizing factors of the two isomers of these compounds. Moreover, for all four compounds (**11**)—(**14**), the equilibrium *Z*:*E* ratios are convincingly higher than those for compounds (**6**)—(**10**) since the *E*-configuration is no longer favoured by conjugation effects.

Table 2. Relevant *X*-ray crystallographic data[3–5,14]



Z-isomer



E-isomer

R = H or Me

Compd.	Dihedral angle (°) (between planes of hydantoin and benzene rings)	Bond angle (°)	C-5 to C-6 bond length (Å)
(*Z*)-(**2**)	5.4	(a) 131.8 (b) 123.0 (c) 132.7	1.328
(*Z*)-(**6**)	45.9	(a) 132.6 (b) 121.9 (c) 131.2	1.332
(*Z*)-(**11**)	84.2	(a) 130.9 (b) 123.2 (c) 128.8	1.299
(*E*)-(**6**)	5.7	(a) 121.6 (b) 133.4 (c) 133.7	1.333
(*E*)-(**11**)	57.1	(a) 124.6 (b) 131.2 (c) 132.0	1.332

A closer examination of the *X*-ray crystallographic data of (*Z*)-(**2**), (*Z*)- and (*E*)-(**6**), and (*Z*)- and (*E*)-(**11**) furnishes supporting evidence for the presence of aromatic $\pi \cdots$ Me attractions. The relevant data extracted from previous determinations[3–5,14] are summarized in Table 2. Compared with (*Z*)-(**2**), the molecule of (*Z*)-(**6**) has not only the expected larger dihedral angle between the planes of the hydantoin and benzene rings but also slightly larger angle (a) and smaller angles (b) and (c) consistent with the interposition of a methyl group at N(1). The molecules of (*Z*)- and (*E*)-(**6**) show inverse relationship of the sizes of angles (a) and (b). In (*Z*)-(**6**), the bulkiness of the neighbouring methyl and phenyl groups enlarges angle (a) at the expense of angle (b), while in (*E*)-(**6**) repulsion between C(4)=O and the *ortho*-H of the nearly co-planar phenyl group enlarges angle (b) at the expense of angle (a) and increases angle (c) at the same time. The internal angle N(1)–C(5)–C(4) of the hydantoin ring remains the same at 105° in both isomers. Unexpectedly, introduction of three bulky methyl groups at 2,4,6-positions in the phenyl ring does not increase but actually decreases the angles (b) and (c) in (*E*)-(**11**) relative to (*E*)-(**6**). This must be the result of twisting the aryl group out of the plane of the hydantoin ring by 57.1°. A more interesting observation is derived from comparison of (*Z*)-(**11**) with (*Z*)-(**6**). Although both molecules have twisted conformations the angles (a) and (c) in (*Z*)-(**11**) are significantly smaller than the corresponding angles in (*Z*)-(**6**) and the length of the exocyclic C=C is shortest among the five compounds whose *X*-ray structures were determined. This strongly suggests that in (*Z*)-(**11**), in spite of being more heavily substituted, the benzene ring with its π electron-density enriched by three methyl substituents is drawn closer to the N(1)–Me group. The larger dihedral angle of 84.2° shows that the benzene and hydantoin rings are almost orthogonal in (*Z*)-(**11**) so that the N(1)–Me group is

Table 3. Melting points and analytical data of compounds (**11**)—(**14**)

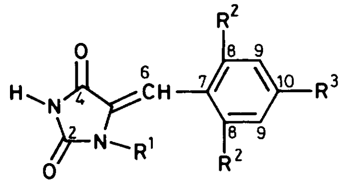
Compd.	M.p./°C (uncorrected)	Found (%) C	H	N	Cl	F	Calc. (%) C	H	N	Cl	F
(*E*)-(**11**)	229—230	68.9	6.8	11.4			68.9	6.6	11.5		
(*Z*)-(**11**)	183—185	68.9	6.7	11.5			68.9	6.6	11.5		
(*E*)-(**12**)	257—259	57.4	5.3	9.5			57.5	5.5	9.6		
(*Z*)-(**12**)	226—228	56.5	5.4	9.4			57.5	5.5	9.6		
(*E*)-(**13**)	245—246	48.6	2.7	10.1	25.9		48.7	3.0	10.3	26.2	
(*Z*)-(**13**)	211—212	48.4	2.7	10.4	26.0		48.7	3.0	10.3	26.2	
(*E*)-(**14**)	230—231	55.2	3.2	11.9		15.9	55.5	3.4	11.8		16.0
(*Z*)-(**14**)	180—181	55.6	3.2	10.7		15.8	55.5	3.4	11.8		16.0

Table 4. Chemical shifts (from Me_4Si) of compounds (**11**)—(**14**); solvent $(CD_3)_2SO$

^1H Shifts

Compd.	N-1-Me	Vinyl H	N-3-H	ArH	Others
(*E*)-(**11**)	3.10	6.27	11.15	6.83(s)	2.13 (*o*-Me), 2.22 (*p*-Me)
(*Z*)-(**11**)	2.48	6.50	11.38	6.90(s)	2.14 (*o*-Me), 2.24 (*p*-Me)
(*E*)-(**12**)	3.04	5.92	10.97	6.21(s)	3.70 (*o*-OMe), 3.80 (*p*-OMe)
(*Z*)-(**12**)	2.70	6.26	11.13	6.28(s)	3.78 (*o*-OMe), 3.81 (*p*-OMe)
(*E*)-(**13**)	3.13	6.24	11.38	7.23—7.56(m)	
(*Z*)-(**13**)	2.64	6.40	11.63	7.35—7.67(m)	
(*E*)-(**14**)	3.11	6.09	11.38	6.95—7.58(m)	
(*Z*)-(**14**)	2.77	6.26	11.56	7.09—7.69(m)	

^{13}C Shifts



Compd.	C-2	C-4	C-5	C-6	C-7	C-8	C-9	C-10	R^1	R^2	R^3
(*E*)-(**11**)	153.9	162.5	129.4	111.7	131.3	136.0	127.7	136.0	25.7	20.0	20.6
(*Z*)-(**11**)	155.2	163.8	128.6	108.7	131.5	136.2	127.7	137.2	27.1	20.0	20.6
(*E*)-(**12**)	153.5	161.9	130.7	90.4	103.5	161.0 (158.7)	104.1	158.7 (161.0)	25.6	55.5	55.3
(*Z*)-(**12**)	155.2	164.2	131.1	90.6	102.0	161.8 (158.5)	102.6	158.5 (161.8)	27.2	55.5	55.6
(*E*)-(**13**)	153.7	161.9	131.5	105.3	133.3	134.4	127.8	129.7	25.8		
(*Z*)-(**13**)	154.9	163.4	131.5	102.6	133.3	134.5	128.0	130.8	27.0		
(*E*)-(**14**)	153.6	161.9	133.6	96.5	129.9 ($^2J_{CF}$ 22 Hz)	160.1 ($^1J_{CF}$ 247 Hz)	111.2 ($^2J_{CF}$ 23 Hz)	111.7	25.8		
(*Z*)-(**14**)	155.3	163.6	134.5	94.4	131.1 ($^2J_{CF}$ 21 Hz)	159.8 ($^1J_{CF}$ 247 Hz)	111.7 ($^2J_{CF}$ 24 Hz)	112.3	27.4		

best oriented for attractive interaction with the aromatic π electrons.

Hence, among the 5-arylmethylenehydantoins, at least three factors may be identified as influencing the relative stabilities and preferences between the *Z*- and *E*-configurations:

(i) Resonance energy which contributes most effectively to stability when the aryl and hydantoin rings are co-planar and therefore conjugated *via* the intervening C=C, as in the *Z*-isomers of (**1**)—(**5**) and the *E*-isomers of (**1**)—(**10**).

(ii) Steric crowding due to close proximity of the N(1) methyl and aryl groups in *Z*-isomers of (**6**)—(**14**) and of the C(4)=O and bulky *ortho*-aryl substituents in the *E*-isomers of (**11**)—(**14**).

(iii) Specific non-bonded interactions which are dependent on the electronic nature and suitable relative orientation of the groups concerned, such as the attractive aromatic π • • • Me interactions in the *Z*-isomers of (**6**)—(**14**).

The melting points and analytical data of the new compounds (**11**)—(**14**) are reported in Table 3 and their n.m.r. data in Table 4. Some interesting and pertinent differences may be noted between the ^1H n.m.r. spectra of compounds (**11**)—(**14**) and those previously reported for compounds (**6**)—(**10**).[1] In the series (**6**)—(**10**), the *ortho*- and *meta*-phenyl protons in the *E*-isomers give well separated doublets, while for the *Z*-isomers these are either much more closely spaced or coalesce into a multiplet or singlet reflecting the near co-planarity of the *E*-configuration and the deshielding effect of the C-4 carbonyl group and twisted conformation of the *Z*-molecule respectively. In the series (**11**)—(**14**) the absence of *ortho*-protons and twisted conformations result in multiplet or singlet phenyl signals for both *Z*- and *E*-isomers. The vinyl protons at C-6 of the *Z*- and *E*-isomers show expected differences according to their spatial relationship and the anisotropic deshielding effect of the carbonyl group at C-4. It is interesting to note that the N-1 methyl protons of the *Z*-isomers of (**11**)—(**14**) are not only more shielded by their proximity to the benzene ring than those of the corresponding *E*-isomers, as expected, but are also more shielded than corresponding protons in the *Z*-isomers of **(6)**—**(10)**. Moreover, the ^{13}C shifts of the N-1 methyl in (*Z*)-**(11)**—(*Z*)-**(14)** are also found at higher field than the corresponding signals in (*Z*)-**(6)**—(*Z*)-**(10)**. This may be interpreted as enhanced anisotropic shielding resulting from the position of this methyl group directly over and close to the benzene ring in (*Z*)-**(11)**—(*Z*)-**(14)**. This is in agreement with the differences in bond angles and bond lengths between (*Z*)-**(11)** and (*Z*)-**(6)** among the above mentioned *X*-ray crystallographic data.

Experimental

Preparations of compounds (*Z*)-**(1)**—(*Z*)-**(10)**, (*E*)-**(1)**, (*E*)-**(6)**—(*E*)-**(10)** have been reported.[1] Compounds **(11)**,**(12)** and **(13)**,**(14)** were prepared by condensations of 1-methylhydantoin with the respective aromatic aldehydes using the piperidine[15] and the acetate[16] methods, respectively. The *Z*- and *E*-isomers were separated by repeated recrystallizations from methanol.

Thermal equilibration was carried out in a Binder Universal Oven with temperature control accurate to ±3 °C. An approximate 3% (w/v) solution of each pure isomer in deuteriated dimethyl sulphoxide in a 5 mm n.m.r. tube was heated in the oven pre-set at the required temperature. At appropriate time intervals, the sample was removed, quickly cooled to room temperature, and its ^{1}H n.m.r. spectrum was measured using a JOEL FX90Q Fourier transform n.m.r. spectrometer. This was repeated until equilibrium was reached. It was assumed that no change occurred during the time taken to obtain the spectrum. Integration of the areas of the signals of the vinyl protons and/or the N-1 methyl protons of the two isomers provided a measure of their relative concentrations and hence the equilibrium composition.

To obtain more accurate equilibrium compositions for compounds **(6)**—**(14)**, which were available in both *Z* and *E* forms, a mixture of the two isomers having composition close to the equilibrium value as estimated above was prepared and heated until the isomeric ratio remained constant within experimental errors. Equilibration was achieved much more quickly with relatively less decomposition.

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References

1 S. F. Tan, K. P. Ang, and Y. F. Fong, *J. Chem. Soc., Perkin Trans. 2*, 1986, 1941.
2 T. B. Johnson and J. S. Bates, *J. Am. Chem. Soc.*, 1915, **37**, 384.
3 M. G. B. Drew, K. F. Mok, K. P. Ang, and S. F. Tan, *Acta Crystallogr., Sect. C*, 1987, **43**, 743.
4 M. G. B. Drew, K. F. Mok, K. P. Ang, and S. F. Tan, *Acta Crystallogr., Sect. C*, 1987, **43**, 745.
5 M. G. B. Drew, K. F. Mok, K. P. Ang, and S. F. Tan, *Acta Crystallogr., Sect. C*, 1987, **43**, 1177.
6 Y. Kodama, K. Nishihata, M. Nishio, and Y. Itaka, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1490.
7 M. Hirota, T. Sekiya, K. Abe, H. Tashiro, M. Karatsu, M. Nishio, and E. Osawa, *Tetrahedron*, 1983, **39**, 3091.
8 M. Hirota, K. Abe, H. Suezawa, and M. Nishio, *J. Mol. Struct.*, 1985, **126**, 455.
9 K. Abe, M. Hirota, and K. Morokuma, *Bull. Chem. Soc. Jpn.*, 1985, **58**, 2713.
10 H. Fujiwara, A. K. Bose, M. S. Manhas, and J. M. van der Veen, *J. Chem. Soc., Perkin Trans. 2*, 1979, 653.
11 H. Fujiwara and J. M. van der Veen, *J. Chem. Soc., Perkin Trans. 2*, 1979, 659.
12 H. Fujiwara, A. K. Bose, M. S. Manhas, and J. M. van der Veen, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1573.
13 Y. Nakai, G. Yamamoto, and M. Oki, *Chem. Lett.*, 1987, 89.
14 M. G. B. Drew, K. F. Mok, K. P. Ang, and S. F. Tan, *Acta Crystallogr., Sect. C*, 1987, **43**, 969.
15 G. Billek, *Org. Synth.*, 1963, **43**, 49.
16 H. L. Wheeler and C. Hoffman, *Am. Chem. J.*, 1911, **45**, 368.

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