

## Energy Barrier for *E-Z* Isomerisation of *N*-Sulphenylimines

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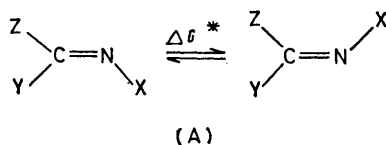
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**Summary** Energy barriers for the *E-Z* isomerisation of a series of *N*-sulphenylimines are interpreted in terms of hyperconjugation involving the nitrogen lone-pair in an inversion mechanism.

Two mechanisms for the *E-Z* isomerisation of imines and their derivatives have been proposed, an inversion at nitrogen and torsion around the C=N bond<sup>1</sup> (A); one of these is controlled by electronic changes in the  $\sigma$ -bond system and the other by  $\pi$ -delocalisation. In this note we discuss the energy barriers ( $\Delta G^*$ ) for *N*-sulphenylimines in terms of a general model for the interaction of the nitrogen lone-pair orbital with orbitals of the substituents. A summary of the more pertinent results of variable temperature n.m.r. measurements of  $\Delta G^*$  is in the Table.



The following major conclusions are drawn from these and other results.

(i) Substitution in the S-Ph group produces small effects on  $\Delta G^*$  [compounds (5)–(7), Table; a series of 4-substituted compounds leads to a Hammett  $\rho$  value of *ca.*  $-0.2$ ].

(ii) Non-conjugating electron-attracting substituents on imino carbon [*e.g.* (3) and (4)] and on sulphur [(9)–(11)] produce relatively large decreases in  $\Delta G^*$  (similar effects have been observed for imines<sup>2</sup>).

(iii) Substitution of alkyl groups by hydrogen [*cf.* (1) and (2)] on the iminyl carbon atom produces large decreases in  $\Delta G^*$ .

(iv) Substitution of *C*-methyl by *C-p*-tolyl produces a relatively small decrease in  $\Delta G^*$  [(2) and (7)].

(v) Replacement of *N*-sulphenyl by *N*-sulphonyl sulphur produces large decreases in  $\Delta G^*$ .

Conversion of nitrogen (local symmetry  $C_{2v}$ ) to nitrogen (local symmetry  $C_\infty$ ) increases the energy, as the  $3a_1$  orbital on nitrogen has a lower energy than the  $1\pi_u$  orbital (Figure). There are two major factors which affect this energy difference: (a) an increase in the electronegativity

TABLE. Free energies of activation,  $\Delta G^*$ , at the coalescence temperature  $T_c$ ,<sup>a</sup> for *N*-sulphenylimines,  $R^1R^2C=NSR^3$ , in deuteriochloroform solution.

Compound	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	$\Delta\nu$ /Hz	$T_c$ /°C	$\Delta G^*/$ (kJ mol <sup>-1</sup> )
(1)	H	H	2-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	18.6	1	56.9
(2)	Me	Me	2,4-(NO <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	2.0 <sup>b</sup>	79 <sup>b</sup>	82.2
(3)	ClCH <sub>2</sub>	ClCH <sub>2</sub>	2-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	1.3 <sup>c</sup>	53 <sup>c</sup>	77.0
(4)	CF <sub>3</sub>	CF <sub>3</sub>	2-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	87.4 <sup>d</sup>	32 <sup>d</sup>	61.5
(5)	4-MeC <sub>6</sub> H <sub>4</sub>	4-MeC <sub>6</sub> H <sub>4</sub>	Ph	5.1	72	77.8
(6)	"	"	2-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	4.0	62	76.4
(7)	"	"	2,4-(NO <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	4.0	67	77.7
(8)	"	"	Me	4.7	69	77.4
(9)	"	"	PhCH <sub>2</sub>	2.7	52	71.1
(10)	"	"	Ph <sub>3</sub> C	6.4	33	68.2
(11)	"	"	Cl <sub>3</sub> C	3.0	-3	61.9
(12)	"	"	PhSO <sub>2</sub> <sup>e</sup>	4.5	-23	56.1

<sup>a</sup> 60 MHz <sup>1</sup>H n.m.r. spectrometry, unless stated otherwise. <sup>b</sup> 100 MHz <sup>1</sup>H n.m.r. spectrometry. <sup>c</sup> 220 MHz n.m.r. spectrometry. <sup>d</sup> 56.4 MHz <sup>19</sup>F n.m.r. spectrometry. <sup>e</sup> *N*-Sulphonylimines. <sup>f</sup> Calculated from  $\Delta G^* = 4.57 T_c [19.13 + \log_{10} \{T_c / (\Delta\nu^2 + 6J_{AB}^2)\}]$ , compound (1),  $J_{AB} = 12.9$  Hz; or  $\Delta G^* = 4.57 T_c [19.13 + \log_{10} \{T_c / \Delta\nu\}]$ , compounds (2)–(11). Values quoted  $\pm 0.8$  kJ mol<sup>-1</sup>.

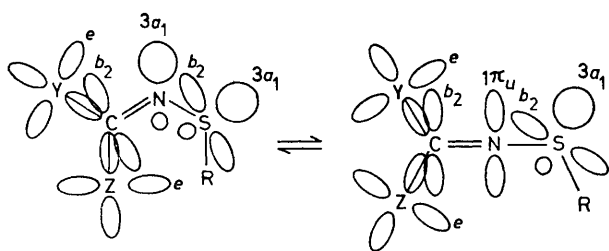


FIGURE. Orbital diagrams for ground- and transition-state geometries.

of the substituent X decreases the energy of the  $3a_1$  orbital relative to the  $1\pi_u$ , consequently increasing the energy difference between the  $C_{2v}$  and  $C_\infty$  configurations; and (b) overlap of the substituent orbitals at X, Y, or Z with the  $1\pi_u$  orbitals of nitrogen will be greater than that with the  $3a_1$  orbital, thus influencing the energy of the  $C_\infty$  configuration more than that of the  $C_{2v}$  form. These two effects may influence  $\Delta G^*$  in opposite directions, leading to complex variations in  $\Delta G^*$  with change in substituent.

Thus, substitution at N and at C by electron attracting groups tends, *via* (a) above, to increase  $\Delta G^*$ , but orbital interactions decrease  $\Delta G^*$  through increased interaction of

$1\pi_u$  with antibonding orbitals of the substituents. Accordingly, the replacement of SMe by  $SCCl_3$ ,  $SCH_2Ph$ , or  $SPh_3$  decreases  $\Delta G^*$  by increasing the  $1\pi_u-2b_2$  interaction (local symmetry on sulphur  $C_{2v}$ ) and decreasing the  $1\pi_u-1b_2$  interaction.<sup>†</sup> The stabilisation is greater when a sulphenyl group is replaced by a sulphonyl group as  $1\pi_u$  interacts strongly with low lying antibonding and  $3d$  orbitals.

Similarly, replacement of  $CH_3$  by  $CF_3$  on imino carbon increases the  $1\pi_u-2b_2$  interaction (local symmetry at carbon  $C_{2v}$ ) and decreases the  $1\pi_u-1b_2$  interaction. Additional effects are produced by interaction of the  $1\pi_u$  orbital with  $1e$  and  $2e$  orbitals on alkyl and trifluoromethyl groups (local symmetry at carbon  $C_{3v}$ ). The net effect is again a decrease in  $\Delta G^*$ . Substitution of hydrogen at imino carbon by an alkyl group increases  $\Delta G^*$  appreciably. This can be explained by the interaction of the  $1\pi_u(N)$  and  $1e(CH_3)$  bonding orbitals resulting in a significant repulsion energy.<sup>‡</sup>

This model can explain most of the substituent effects observed for imines and their derivatives.<sup>1</sup> Even the low barriers observed for imino-carbonates<sup>4</sup> and guanidines,<sup>5</sup> which have been explained by the torsional mechanism can be explained in this way.

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<sup>†</sup> These interactions can be evaluated in principle by perturbation theory (A. Imamura, *Mol. Phys.*, 1968, **15**, 225; L. Salem, *J. Amer. Chem. Soc.*, 1968, **90**, 543). The main problem is the treatment of the Hamiltonian and in evaluating energies of A.B.O.'s. The symmetry notation given by Gimarc is used (B. M. Gimarc, *J. Amer. Chem. Soc.*, 1971, **93**, 593).

<sup>‡</sup> Estimated as 17.6 kJ mol<sup>-1</sup> per methyl group with a 2-centre overlap integral of 0.10.

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