Z–E Isomerisation of *N*-Sulphenylimines

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The free energies of *Z–E* isomerisation of a wide range of symmetrical *N*-sulphenylimines have been measured at the coalescence temperature by a ^{1}H n.m.r. procedure. In two cases the rate of isomerisation of unsymmetrical *N*-sulphenylimines at a series of temperatures has been measured and activation enthalpies and entropies determined. The effect of substituents on the isomerisation barrier ΔG^* has been interpreted by the hyperconjugation of the nitrogen lone pair with substituents on imine carbon and on nitrogen in a linear transition state adopted for the inversion process. The results are discussed in orbital terms using an extended Hückel perturbation approach, which can be used to interpret qualitatively the effect of substituents on the inversion barrier of a wide range of imino compounds, including guanidines and imino carbonates.

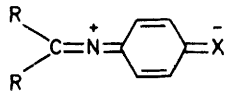
INVERSION at nitrogen has been widely investigated from both an experimental and a theoretical point of view.[1] Whereas the barriers for inversion of pyramidal nitrogen are very low, unless the atom is incorporated in a small ring, imines are generally configurationally stable at ordinary temperatures.[2] This difference is in accord with Walsh's rules [3] which predict larger barriers for the sp^2–sp change at nitrogen than for the sp^3–sp^2 change.

Consequently, quantitative studies of the *Z–E* isomerisation barrier for imines have been largely restricted to compounds with strong conjugating groups at nitrogen,[2] in particular aryl groups, and at iminyl carbon, *e.g.* alkoxy and amino groups, which perturb the π-system appreciably.

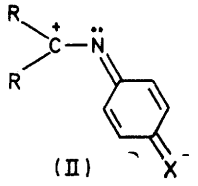
The barriers for imine derivatives cover a very wide range, *e.g.* from >40 for oximes to <10 kcal mol^{-1} for *N*-acyl- and *N*-sulphonyl-imines.[2] In general the effect of an atom substituted at nitrogen is similar for pyramidal and trigonal nitrogen *viz.*, RO > Cl > Br > R_2N >alkyl > aryl ≃ RS, and is usually explained by the increase in electronegativity which stabilises the non-planar and non-linear forms.

The problem is more complex for imines than for amino compounds as several alternative mechanisms are possible for the isomerisation, notably inversion at nitrogen, torsion of the C=N bond, and a combined inversion–torsion process. In order to investigate the mechanism, most studies have been based on the effect of substituents on ΔG^* or ΔH^*, the free energy or enthalpy of activation. The main difficulty in interpreting the results is that a particular substituent may affect ΔG^* for the inversion and torsion processes in the same direction. This is because delocalisation of the nitrogen lone pair in a linear transition state, appropriate to the inversion mechanism and π-delocalisation necessary to promote the torsion mechanism may be affected similarly by a particular substituent.

For example in the case of N-arylimines [4] (I) and (II)



(I)



(II)

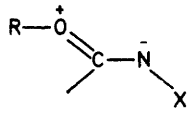
the electron-withdrawing groups X decrease the barrier, which may be explained by invoking either structure (I) or (II). The same situation arises with *N*-acyl- [5] and *N*-sulphonyl-imines.[6]

A decision has to be made therefore between the two extreme mechanisms, torsion and inversion, by considering the magnitude of the substituent effect at nitrogen, the co-operative influence of substituents at the imino carbon atom, and the effect of steric repulsions on the barrier.

Recent work by Jennings *et al.*[7] on the barriers for *Z–E* isomerisation of *N*-alkylimines has shown that increasing the size of the alkyl group produces appreciable decreases in ΔG^* (and ΔH^*), in agreement with earlier indications of such a steric effect. Moreover substitution in phenyl groups substituted at the iminyl carbon atom has a small effect [4] on ΔG^*, in contrast to the large effect observed in the isomerism of aryl-substituted ethylenes involving a torsional mechanism.[8]

Both these observations are therefore in agreement with the inversion mechanism.

On the other hand the substitution of alkoxy and amino groups at the imino carbon atom leads to low barriers for imino carbonates,[9] guanidines,[5] and similar compounds. As these groups conjugate strongly with the C=N double bond, the large decreases in ΔG^* indicate a torsional mechanism, or at least a contribution from



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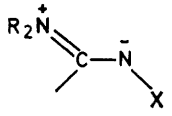


(IV)

the cannonical forms (III) and (IV). However, the effect of X on the barrier is similar to that observed for imines,[2] and also for pyrrolidines [10] (see Table 1).

An inversion mechanism cannot therefore be ruled out, and the large effect of the alkoxy and amino substituents may be due to a change in electronegativity of nitrogen produced by the electron release [(III) and (IV)]. At the end of this paper we suggest an additional stabilisation of the linear transition state due to increased hyperconjugation.

We have found [11] that substitution of sulphur at

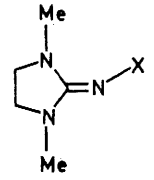
nitrogen produces a large decrease in ΔG^*, as in the case of aziridines, in line with the low electronegativity and possible influence of 3*d* or other polarisation orbitals in stabilising the transition state.

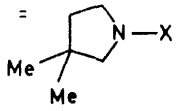
The isomerisation rates are within the n.m.r. time scale [12,13] and the barriers of a large range of compounds (within 13—21 kcal mol^{-1}) can be studied conveniently.

TABLE 1

Variation of the energy barriers in variously substituted imines and amines

Substituent X	ΔG^*(A)[5]/ kcal mol^{-1}	Substituent X	ΔG^*(B)[10]/ kcal mol^{-1}
OMe	23.2	OH	13.0
NMe_2	21.0	ND_3	8.5
CH_2Ph †	11.7	CD_3	7.4

A = 

B = 

† Compare *p*-ClC_6H_4(Ph)C=NMe, $\Delta G^* = 25.5$ kcal mol^{-1}.[4]

RESULTS

(a) *Symmetrical Sulphenylimines.*—Most of the measurements were made with symmetrically substituted sulphenylimines by following the coalescence of the ^{1}H n.m.r. peaks of a suitable substituent (usually a CH_3 or CH_2 group) as the temperature was increased.

The rate constant at coalescence, k_c, is related by expression (1),[14,15] where τ is the mean lifetime of a configuration,

$$k_c = 1/2\tau = \pi\Delta\nu/\sqrt{2} \qquad (1)$$

and $\Delta\nu$ is the peak separation (in Hz) in the absence of exchange. The free energy of activation ΔG^* is given by the Eyring equation (2) where k_B is the Boltzmann constant, *h*

$$k_c = K\left(\frac{k_B T_c}{h}\right)\exp -\Delta G^*/RT_c \qquad (2)$$

Planck's constant, and *K* the transmission coefficient (assumed to be unity).

Combination of equations (1) and (2) gives (3).

$$\Delta G^* = 4.57\ T_c\ (9.97 + \log_{10} T_c/\Delta\nu) \qquad (3)$$

Modifications to this procedure were made when necessary. The spectrum of *N*-(2-nitrothiophenyl)methyleneamine (1) below its coalescence temperature displayed a quartet as a result of AB coupling of the geminal protons. The value of the coupling constant *J* was found to be 12.9 Hz which compares with those of similar compounds. $\Delta\nu$ was calculated as for a coupled AB system. The value of the free energy ΔG^* was calculated from equation (4) as recommended by Lehn and Wagner [10] and tested by Raban *et al.*[13]

$$\Delta G^* = 4.57\ T_c\left[9.97 + \log_{10}\frac{T_c}{(\Delta\nu^2 + 6J^2)^{\frac{1}{2}}}\right] \qquad (4)$$

N-(2,4-Dinitrothiophenyl)-1-isopropyl-2-methylpropylideneamine (3) gave a pair of 1 : 1 doublets due to the coupling of the methyl protons with the methine proton, below the coalescence temperature.

The $^4J_{FF}$ coupling normally seen with fluorine substituted compounds was also observed in the low temperature ^{19}F spectra of *N*-(thiophenyl)- and of *N*-(2-nitrothiophenyl)-2,2,2-trifluoro-1-trifluoromethylethylideneamine. The latter at temperatures just below coalescence gave two broad peaks which, at lower temperatures resolved into two 1 : 3 : 3 : 1 quartets with J_{FF} 6.2 Hz (*cf.* 6.0 Hz for 2,2,2-trifluoro-1-trifluoromethylethylideneamine [14]). The much smaller chemical shift difference in the low temperature spectrum of the *N*-(thiophenyl) analogue led to a more complex second-order spectrum, from which an approximate value of $^4J_{FF}$ of 6.0 Hz was estimated.

Errors in the evaluation of ΔG^* may arise in the measurements of the chemical shift in the absence of $\Delta\nu$, and in the estimation of the coalescence temperature T_c. Inaccuracies in the measurement of $\Delta\nu$ (estimated within the range 0.1—0.4 Hz) have little effect on ΔG^*, *e.g.* a change in $\Delta\nu$ from 4.0 to 6.0 Hz at 300 K changes ΔG^* from 16.2(4) to 16.0(0) kcal mol^{-1}.

Inaccuracies in T_c lead to greater deviations, *e.g.* for $\Delta\nu = 4$ Hz, $\Delta G^* = 16.1(3)$, 16.1(8), 16.2(9), and 16.3(5) kcal mol^{-1} at 298, 299, 301, and 302 K, respectively. As we estimate the maximum error in T_c, obtained by the usual extrapolation procedures, to be $\pm 1°$, an error of ± 0.06 kcal mol^{-1} is obtained. In the most extreme case where $\Delta\nu = 1.3$ Hz and T_c 274 K the maximum error is found to be 0.25 kcal mol^{-1}.

The values of ΔG^* determined from the coalescence temperatures are recorded in Table 2. Examination of the data shows several general features, which may be summarised as follows. (1) Substitution in the SPh group has little effect on ΔG^*. Thus a comparison of compounds (6)—(10) and (11)—(15) show that electron-releasing groups decrease ΔG^* slightly, the change from 4-NO_2 to 4-MeO being only 0.3 and 0.4 kcal mol^{-1}. These give a value of the Hammett ρ parameter of *ca.* -0.2. On the other hand substitution of a 2-NO_2 group appears to decrease ΔG^* slightly (by *ca.* 0.3 kcal mol^{-1}). (2) In contrast, substitution at the iminyl carbon and sulphur atoms produces relatively large changes in ΔG^*. In both cases, electron-attracting groups reduce the isomerisation barrier as shown in Table 3.

These data can be examined in a conventional manner by relating the rate of isomerisation (calculated at a given temperature, by assuming ΔS^* 0 †), to an appropriate linear free energy parameter, since $\Delta G^* = \Delta H^* = E_a + RT$ and $\ln k_1/k_2 = -E_a(T_1 - T_1)/RT_1T_2$. For non-conjugating substituents the Taft σ^* parameter is appropriate, and an approximately linear relationship (ρ^* 0.78, *r* 0.93) is found for the plot of log *k* against σ^* for substitution at sulphur.

There is no doubt that steric parameters affect the rate in some cases, *e.g.* the rate constant is greater for the SBu^t substituted compound than for the SMe compound, but this is probably small compared with the electronic effect (as evidenced by the large difference in rate for $SCCl_3$ and $SCMe_3$ compounds).

No correlation is found between the rate constant and σ^* for the *C*-iminyl substituted compounds. However, some correlation was found when polar and steric effects were separated according to the procedure of Pavelich and Taft.[15] The appropriate equation (5) where ρ^* and σ^* are polar

$$\log k = \rho^*\sigma^* + \delta E_s + \text{constant} \qquad (5)$$

† As has been found by other workers [7] for similar systems some unsymmetrical derivatives of these compounds have been shown to have values for the entropy of activation close to zero (see Table 4).

TABLE 2

Free energies of activation ΔG^* at the coalescence temperature for the symmetrical *N*-sulphenylimines $R^1{}_2C{=}NSR^2$ in deuteriochloroform at 60 MHz

Compound	R^1	R^2	$\Delta\nu$ [a]/Hz	T_c/°C	ΔG^*/kcal mol^{-1}
(1)	H	2-$NO_2C_6H_4$	18.6	1	13.6
(2)	CH_3	2,4-$(NO_2)_2C_6H_3$	2.0 [b]	73	19.3
(3)	Pr^i	2,4-$(NO_2)_2C_6H_3$	2.8	92	20.2
(4)	$C_6H_5CH_2$	2-$NO_2C_6H_4$	10.1	107	20.1
(5)	$C_6H_5CH_2$	2,4-$(NO_2)_2C_6H_3$	10.0	113	20.4
(6)	4-$CH_3C_6H_4$	4-$NO_2C_6H_4$	4.8	75	18.8
(7)	4-$CH_3C_6H_4$	4-ClC_6H_4	4.9	72	18.7
(8)	4-$CH_3C_6H_4$	C_6H_5	5.1	72	18.6
(9)	4-$CH_3C_6H_4$	4-$CH_3C_6H_4$	4.6	70 [e]	18.6
(10)	4-$CH_3C_6H_4$	4-$CH_3OC_6H_4$	5.6	69.5	16.5
(11)	4-$CH_3C_6H_4$	2,4-$(NO_2)_2C_6H_3$	4.0	67	18.5
(12)	4-$CH_3C_6H_4$	4-Cl,2-$(NO_2)_2C_6H_3$	4.2	63	18.2
(13)	4-$CH_3C_6H_4$	2-$NO_2C_6H_4$	4.0	62	18.2:
(14)	4-$CH_3C_6H_4$	4-CH_3-2-$NO_2C_6H_3$	4.0	62 [e]	18.2
(15)	4-$CH_3C_6H_4$	4-CH_3O-2-$NO_2C_6H_3$	4.5	62	18.1
(16)	4-$CH_3C_6H_4$	Cl_3C	3.0	−3	14.8
(17)	4-$CH_3C_6H_4$	$(C_6H_5)_3C$	6.4	33	16.3
(18)	4-$CH_3C_6H_4$	$C_6H_5CH_2$	2.7	52	17.0
(19)	4-$CH_3C_6H_4$	CH_3	4.7	69	18.5
(20)	4-$CH_3C_6H_4$	$(CH_3)_3C$	4.0	57.5	18.0
(21)	4-$CH_3C_6H_4$	$(CH_3C_6H_4)_2C{=}N$	4.3	−17	13.8
(22)	$ClCH_2$	2-$NO_2C_6H_4$	1.3 [c]	53	18.4
(23)	CF_3	2-$NO_2C_6H_4$	87.4 [d]	32	14.7
(24)	CF_3	C_6H_5	16.9 [d]	6	14.3

[a] Peak separation in the absence of exchange. [b] Determination at 100 MHz. [c] Determination at 220 MHz. [d] Determination at 56.4 MHz (^{19}F n.m.r.). [e] Difficult to assess due to overlap of absorption by CH_3 group on R^2.

reaction and substituent constants respectively and δ and E_s are steric reaction constants and substituent constants, can be applied to the data using a least squares procedure. The steric and polar constituents of the rate constant were calculated in this way, and log $-\rho^*\sigma^*$ plotted against E_s and log $k - \delta E_s$ plotted against σ^*. The graphs are approximately linear giving values of ρ^* 1.6 (r 0.96) and δ 2.4 (r 0.95). This indicates that both steric and polar factors influence the rate of isomerisation, although the correlation is poor, and a four parameter equation tends to mask important factors by minimising the deviations by the reiterative adjustment of the parameters.

TABLE 3

Isomerisation barriers

Substitution at iminyl carbon

	Pr^i	$PhCH_2$	CH_3	$ClCH_2$	Ph	CF_3	H
ΔG^*/kcal mol^{-1}	20.2	20.1 (20.4)	19.3	18.4	18.2 (18.5)	15.7	13.6

Substitution at sulphur

	CMe_3	CH_3	CH_2Ph	CPh_3	CCl_3	$N{=}CPh_2$
ΔG^*/kcal mol^{-1}	18.0	18.5	17.0	16.3	14.8	13.8

(b) *Unsymmetrical* N-*Sulphenylimines*.—With two different groups substituted at the imino carbon atom two isomers could in principle be isolated by classical means. However if the energy barrier between the two forms is suitable, equilibration between them may be followed by n.m.r. measurements. The concentration of each isomer at a given temperature can be observed directly from the spectra and the rate of approach to equilibrium calculated using normal kinetic procedures.

In the cases studied here equal concentrations of the isomers were observed at equilibrium, and hence the rate constant for isomerisation was equal to half the slope of the linear first-order plot.

The rate constants together with the experimental activation energies E_α obtained from the Arrhenius equation and values of ΔH^* and ΔG^* calculated from the absolute rate equations are recorded in Table 4.

TABLE 4

Variation of rates with temperature and calculated activation parameters for the isomerisation of two unsymmetrically substituted *N*-sulphenylimines C_6H_5-(p-$CH_3C_6H_4$)C=NC_6H_3-4-Cl-2-NO_2 (A) and C_6H_5-(p-$CH_3C_6H_4$)C=NC_6H_4-2-NO_2 (B)

(A)

T/°C	k_1/s^{-1}	r
−32.5	2.98×10^{-4}	0.990
−29.8	4.11×10^{-4}	0.986
−26.2	8.61×10^{-4}	0.989
−22.8	1.18×10^{-3}	0.986
57.5 [a]	8.89	

E_a 19.45, ΔG^* 18.0, ΔH^* 18.80 kcal mol^{-1}, ΔS^* +2.4 cal K^{-1} mol^{-1} [b]

(B)

T/°C	k_1/s^{-1}	r
−33.1	2.23×10^{-4}	0.981
−28.8	4.69×10^{-4}	0.985
−25.8	8.15×10^{-4}	0.971
−22.8	1.34×10^{-4}	0.946
59.0 [a]	9.33	

E_a 19.45, ΔG^* 18.0, ΔH^* 18.85 kcal mol^{-1}, ΔS^* +2.6 cal K^{-1} mol^{-1} [b]

[a] Value from the coalescence point. [b] Calculated for the coalescence temperature.

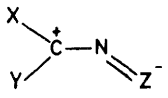
DISCUSSION

The interpretation of the isomerisation process of imines is complicated by the possibility of several mechanisms, in particular inversion, torsion, and a combined inversion–torsion process. Theoretical calculations are too imprecise at the semi-empirical [16] level to account for even the major changes in ΔG^* produced by changing the atom substituted at nitrogen and *ab initio* methods have

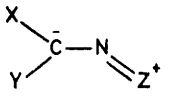
been used [17] only for the simplest molecules, *e.g.* HC_2=NH, for which no experimental data are available.

Arguments in favour of a particular mechanism have to be drawn from the effects of substituents and of the medium on the energy barrier. It is generally agreed that in the absence of strongly conjugating groups, the barrier for rotation of the C=N bond is considerably higher than the observed values. Analogy can be drawn with the rotational energy of C=C double bonds which changes from the value of 65.0 kcal mol^{-1} for ethylene [18] to values within the n.m.r. range, <10 kcal mol^{-1}, when strong electron-attracting or -releasing groups are substituted.[19] The changes in ΔG^* follow the well established conjugating power of the substituents in an olefin,[2] *e.g.* Ph < CN < COOR < COPh < $COCH_3$ and R_2N > RO > RS > alkyl.

These changes in ΔG^* for imines can be interpreted in classical terms involving the participation of two canonical forms (V) and (VI) in the transition state.



(V)



(VI)

The barrier is reduced [2] when Z = aromatic, RCO, and RSO_2, and when X,Y = R_2N and RO, and hence in these cases there is an argument in support of the torsional process. However, as pointed out by Kessler [20] and others, these reduced barriers can be explained also by assuming an inversion mechanism, which has the advantage of explaining, qualitatively, the other major changes in ΔG^*. The model we shall discuss below also provides an explanation on the basis of the inversion mechanism of the low barriers observed for imino carbonates, guanidines, and structurally related molecules.

The low barriers for *N*-sulphenylimines (14—20 kcal mol^{-1}) [6b,11] compared with oximes (>40 kcal mol^{-1}), cannot be explained by the torsional mechanism, since the participation of the canonical form (VI) should be greater for oxygen than for sulphur. A similar reduction in barrier is observed for three-co-ordinated nitrogen, as in *N*-substituted aziridines,[21] where the inversion mechanism is operative. Reference to the data in Table 2 shows that electron attracting substituents (*e.g.* Ph_3C, CCl_3) produce significant decreases in ΔG^*.

These substituents reduce the energy of the sulphur 3*p* orbital involved in π-conjugation with the imino group, and hence an increase in ΔG^* should be observed for a torsional process. The reverse is the case. Conjugating substituents in the SPh group have little effect on ΔG^*. Although electron-withdrawing substituents in the 4-position produce slight decreases in ΔG^* (Hammett ρ *ca.* −0.2), the barrier for the unsubstituted compound is equal to that of the 2,4-dinitro compound where the sulphur 3*p* lone-pair is strongly conjugated. These observations show that the canonical form (VI) does not participate in the transition state structure.

A torsional mechanism could be promoted by an increase in the contribution of the canonical form (V). Again the large difference in ΔG^* for *N*-sulphenylimines and oximes cannot be explained in this way, unless a very large contribution from the 3*d* orbitals of sulphur can produce a decrease in energy of the order of 20 kcal mol^{-1}. Such a participation is contrary to all theoretical predictions at this time.[22]

The effect of substituents at the imino carbon atom on ΔG^* (Table 2) also discounts participation from structure (V). Thus substitution of hydrogen by an alkyl group produces a large increase in the barrier energy, whereas electron-attracting substituents (*e.g.* CF_3, CH_2Cl) produce lower values of ΔG^* than do alkyl substituents. Moreover, substitution of a *C*-methyl group by *C*-*p*-tolyl produces only a small decrease * in ΔG^*, more in accord with a change in electronegativity of imino carbon, than with delocalisation as required by (V) or (VI).

The present data therefore provide no evidence in favour of a torsional mechanism and the data in Table 2 will now be analysed in terms of the alternative inversion mechanism. According to this, the barrier, ΔG^*, is determined primarily by the energy difference between the $3a_1$ orbital on nitrogen (local symmetry C_{2v}) and the $1\pi_u$ orbital (local symmetry C_∞) on nitrogen in the 'linear' transition state,† following Walsh's rules.[3] This energy difference increases with the electronegativity (Coulomb integrals) of the atoms substituted on nitrogen. Alternatively, this can be regarded as a change from sp^2 hybridised nitrogen to *sp* nitrogen, but this interpretation is not particularly useful when the effect of substituents is considered.

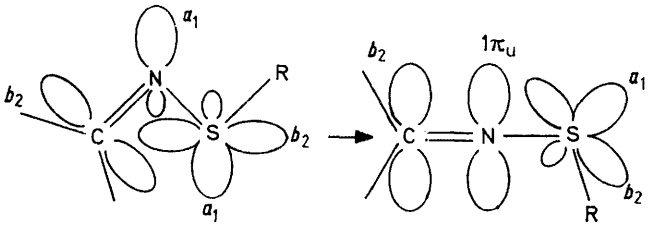


FIGURE 1 Spacial orientation of relevant orbitals in the ground and transition states of *N*-sulphenylimines

Accordingly, electron-withdrawing substituents which increase the electronegativity of the carbon and sulphur atoms should increase the inversion barrier.[1] The reverse is the case and consequently other factors must dominate the changes in activation energy. The simplest way of analysing these effects qualitatively is to consider the effect of orbitals on the substituents on the $3a_1$(N) ground state and $1\pi_u$(N) transition state 'lone pair' orbitals as perturbations ‡ (see Figure 1).

Since the $1\pi_u$(N) orbital is essentially non-bonding (2*p*), it will interact more strongly with the substituent orbital

* Electron-attracting substituents in the 4-position reduce ΔG^* slightly (ρ +0.4 with a low correlation coefficient).

† The group theoretical formalism given by Gimarc [23] is used.

‡ The appropriate equations are given by Imamura [24] and by Salem [25] (see Appendix).

than does $3a_1$(N) ground state orbital, as this is bonding with a reduced coefficient on nitrogen.

Adopting the orbital model, σ-electron-withdrawing substituents on sulphur and on imino carbon can be treated in the same way. For the purposes of discussion we consider the replacement of CH_3 by CF_3 on imino carbon, and of CMe_3 by CCl_3 on sulphur. These examples are chosen as steric differences should be minimal.

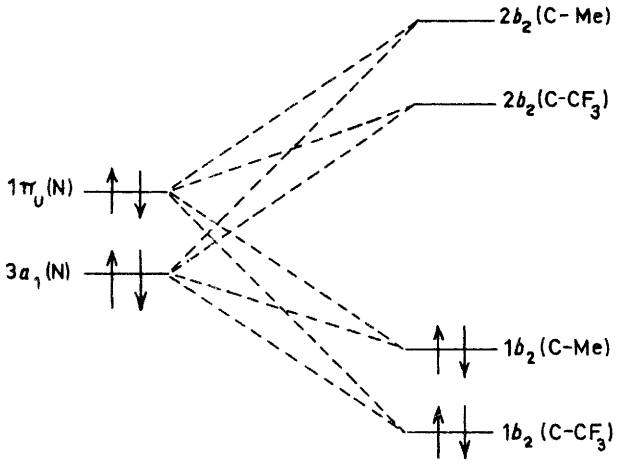


FIGURE 2 Perturbation of orbitals of the Me and CF_3 groups substituted at the iminyl carbon atom of an *N*-sulphenylimine by the lone pair orbitals in bent ($3a_1$) and linear (π_u) forms

The replacement of CH_3 by CF_3 reduces the energy of the corresponding bonding and anti-bonding orbitals (b_2 with local symmetry on imino carbon C_{2v}). As shown in the diagram (Figure 2) this increases the interaction of the $1\pi_u$(N) orbital with the $2b_2$ (anti-bonding) orbital and decreases the interaction with the $1b_2$ (bonding orbital), thus leading to a decrease in energy of the transition state.

Moreover the coefficient on imino carbon in $2b_2$ is greater when CF_3 is substituted, but less in the $1b_2$ orbital. Thus both orbital coefficients and orbital energies lead to a reduction in the energy of the $1\pi_u$(N) orbital on perturbation by the b_2 type orbitals of the CF_3 group.

A similar reduction in energy of the ground state also occurs on substitution of a CH_3 group by a CF_3 group by the interaction of the $3a_1$(N) orbital with adjacent *b* type orbitals (Figure 2), but this is less than the reduction produced by perturbation of the $1\pi_u$ orbital in the transition state for reasons given above. This explanation is equivalent to the statement that a $2p$ lone pair is hyperconjugated with an adjacent group more strongly than an sp^2 lone pair.

The same argument holds for substitution at sulphur.

* The interaction $1\pi_u$(N)–$2b_2$(S) is equivalent to the n–σ* interaction ('negative hyperconjugation') proposed by M. Raban and D. Kost, *J. Amer. Chem. Soc.*, 1972, **94**, 3234.

† A referee has pointed out that the low ΔG^* value for compound (1) may be due to traces of impurity, particularly acid, in the solvent (*cf.* ref. 4). Although this remains as a possibility, detailed studies of the solvent effect for similar compounds gave no evidence of acid catalysis.

The local symmetry at sulphur is also C_{2v} (though orientation with respect to the C–N–S system is of course different), and similarly, increased interaction * of $1\pi_u$(N) with $2b_2$(S) and decreased interaction with $1b_2$(S) on the introduction of electron-attracting substituents, *e.g.* CCl_3, CPh_3, occurs resulting in a decrease in ΔG^*.

The substitution of alkyl groups for hydrogen atoms at the imino carbon atom produces large increases in the inversion barrier. Steric interaction with the substituents should lead to a decrease in ΔG^* as has been found in certain cases where bulky groups are substituted.[7]

The increase in ΔG^* must therefore be due to an increase in steric hindrance or to an increase in inter-electronic repulsion on formation of the transition state.†

According to the above model, substitution of an alkyl group for hydrogen introduces a set of *e*-type orbitals (local symmetry of methyl carbon is C_{3v}) which can overlap with the b_2 orbitals on the imino carbon (Figure 1) atom and with the $1\pi_u$(N) orbital (Figure 3). The *e* orbitals ‡ of an alkyl group are of high energy and hence the major perturbation introduced is the $1e(CH_3)$–$1\pi_u$(N) interaction which is repulsive. These interactions are not negligible, *e.g.* using a simple one electron extended Hückel treatment § values of this repulsion energy of 8.3, 5.3, and 3.0 kcal mol^{-1} are found for overlap integrals [S_{ij}, equation (10)] of 0.10, 0.08, and 0.06. These are difficult to evaluate accurately but Slater orbital calculations show that the overlap $1e$–$1\pi_u$ is in this range.

According to this model, changes in ΔG^* are produced mainly by the interaction of the nitrogen lone pair with the electrons in the σ-bond framework of the substituents.

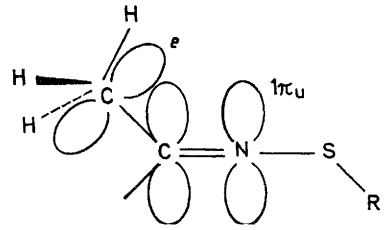


FIGURE 3 Diagrammatic representation of the overlap of orbitals on an imino methyl group with $2p$ lone pair orbital on nitrogen ($1\pi_u$) in the linear transition state

Consequently changes in the π-bond system have little effect on ΔG^*. Thus a change from a methyl to a *p*-tolyl group on imino carbon produces a small decrease in ΔG^* which can be accounted for by increased delocalisation of a lone pair into the $1b_2$ orbital of the imino carbon atom which is modified by the electronegative *p*-tolyl group. Similar observations have been made for imines, in which the replacement of *C*-methyl [26] by *C*-aryl groups [27] produces a small decrease in ΔG^*. Moreover substitution in the 4-position of *C*-aryl- [27] and

‡ Anti-bonding orbital of π-type symmetry of a CH_3 group.

§ This cannot give accurate values in view of the extreme simplicity of the theory, but since the empirical parameter (k) is used to lead to reasonable bond energies, the estimate is of a correct order of magnitude (see Appendix).

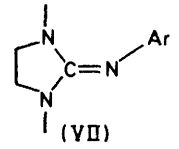
C-alkyl-imines [7] also produces negligible changes in the barrier energy.

Applications to Other Systems.—Substitution of amino and alkoxy groups at the imino carbon atom produce large decreases in ΔG^* which have been taken as evidence for the torsional mechanism.[28] There is no doubt that these groups modify the π-system considerably, but this does not necessarily prove that the energy of the C=N π bond is reduced to a value commensurate with ΔG^*. In an extensive series of investigations, Kessler [2] has shown that this conjugation could reduce the inversion barrier and other workers have proposed an inversion–torsion mechanism.[6a] It is reasonable to assume that strong conjugation leading to a negatively charged imino nitrogen atom would lead to a change in configuration at nitrogen as the two *p* orbitals become degenerate.

On the basis of our earlier discussion, we propose a different electronic stabilisation to account for these low barriers. As in the case of *N*-sulphenylimines the substitution of CF_3 groups for methyl groups at the imino carbon atom decrease the barrier of imines,[29] *e.g.* $Me_2C{=}NPh$,[26] ΔG^* 20.3; $(CF_3)_2C{=}NPh$,[29] ΔG^* 15.4; $(MeO)_2C{=}NPh$,[9] ΔG^* 14.3 kcal mol^{-1}, to a value similar to that of the corresponding imino carbonate. Since methoxy groups are strongly electron attracting in the σ-bond framework we suggest that the stabilisation of the transition states is due to the same electronic effect. The $1\pi_u$ orbital on nitrogen can interact strongly with the $2b_2$ orbital on the α-carbon of the methoxy and CF_3 substituted imines.

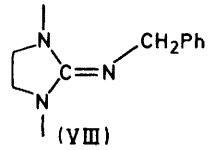
A similar stabilisation by electronegative groups has been proposed to explain the gauche [30] and anomeric [31] effects, where an alkoxy group reduces the energy by 3—4 kcal mol^{-1} compared with a methyl group.

Moreover conjugation in the π-system decreases the electron density on oxygen reducing further the energy of the $2b_2$ orbital and increasing the orbital coefficient on carbon. This leads to the idea that π-conjugation involving heteroatoms increases the hyperconjugation in the opposite sense. This 'negative' hyperconjugation [32] would be greater for *C*-substituted amino groups leading to the low observed ΔG^* values for *N*-substituted guanidines. Indeed the reported barriers for *N*-alkyl- and *N*-phenyl-guanidines are very similar,[9a] *e.g.* (VII) and (VIII), indicating that the conjugation into the *N*-aryl



(VII)

ΔG^* 12 kcal mol^{-1}



(VIII)

ΔG^* 12 kcal mol^{-1}

group is suppressed by extensive delocalisation of the $1\pi_u$ orbital into groups substituted at imino carbon. This competition could explain the minima found in Hammett plots,[33] as strong electron-attracting groups in the *N*-aryl group could compete with the imino carbon substituent for the $1\pi_u$ electrons, whereas electron-releasing groups could augment the delocalisation in the reverse direction.

EXPERIMENTAL

Preparation of Reactants.—The following sulphenyl chlorides were prepared by the action of chlorine in tetrachloromethane on the corresponding thiol according to the standard procedure: 2-nitrobenzene- (52%), m.p. 74.5—75.5° (lit.,[34] 75°); 2,4-dinitrobenzene- (50%), m.p. 94—97° (lit.,[35] 95—96°); 4-chloro-2-nitrobenzene- (83%), m.p. 95° (lit.,[36] 98°); 4-methyl-2-nitrobenzene- (82%), m.p. 86—88° (lit.,[37] 90°); 4-methoxy-2-nitrobenzene- (46%), m.p. 104—106° (lit.,[38] 106—108°); benzene- (55.5%), b.p. 87—90° at 12 mmHg (lit.,[39] 73—75° at 9 mmHg); 4-methoxybenzene- (84%), b.p. 88—92° at 0.1 mmHg (lit.,[40] 128—130° at 17 mmHg); 4-nitrobenzene- (82%), m.p. 52° (lit.,[41] 52°). Phenylmethane-, methane-, 2,2-dimethylethane-, toluene-*p*-, and 4-chlorobenzene-sulphenyl chlorides were prepared similarly but were not isolated from solution. Triphenylmethanesulphenyl chloride (54%) was prepared by the action of chlorine on triphenylmethanethiol in ether at ambient temperature for 3 h, m.p. 136—138° (lit.,[42] 137°). Trichloromethanesulphenyl chloride was obtained from Koch–Light.

2-Nitrobenzenesulphenamide (72%) was prepared by the action of 2-nitrobenzenesulphenyl chloride on ammonia in dichloromethane at ambient temperature for 1 h, m.p. 125—126° (lit.,[43] 124—126°). 2,4-Dinitrobenzenesulphenamide (60%) was prepared similarly, m.p. 120—121° (lit.,[44] 119—120°).

The following imines were prepared by the procedure of Pickard and Tolbert,[45] involving the reaction between a Grignard reagent and nitrile and subsequent treatment with methanol: diphenylmethyleneamine (65%), b.p. 100° at 0.5 mmHg (lit.,[18] 127° at 3.5 mmHg); di-4-tolylmethyleneamine (61%), b.p. 130—135° at 0.2 mmHg (lit.,[46] 162° at 3 mmHg); phenyl-4-tolylmethyleneamine (49%), b.p. 115—120° at 0.1 mmHg, b.p. 115—120°, $\nu_{max.}$ 3 275 cm^{-1} (N–H), δ 2.35 (3 H, s), 7.1—7.7 (9 H, m), and 9.5 (1 H, s). 2,2,2-Trifluoro-1-trifluoromethylethylideneamine was kindly supplied by Dr. M. Green.

Preparation of Sulphenylimines.—Two general methods were used for the preparation of the *N*-sulphenylimines, with modifications depending on the structure of the reactants.

(1) The condensation of the appropriate sulphenamide and ketone according to the method of Zincke and Farr [47] was used to prepare several *N*-sulphenylimines.

(1a) This method was modified in certain cases, by boiling the sulphenamide and ketone in benzene for 72 h in a Dean and Stark apparatus to remove water produced by the condensation reaction, and subsequently removing the solvent and crystallising the residue from benzene–hexane (1 : 9).

These procedures could be used with aliphatic ketones only.

(2) Most *N*-sulphenylimines were prepared by the action of the imine on the appropriate sulphenyl halide. In a typical experiment, 1,1-diphenylmethyleneamine (1.8 g) and triethylamine (1.0 g) in sodium-dried benzene (50 ml) were treated with 2-nitrobenzenesulphenyl chloride (1.9 g) in benzene (10 ml). The mixture was stirred at ambient temperature for 1 h and the precipitate of amine hydrochloride filtered off. Solvent was removed from the filtrate and the residue recrystallised twice from hexane–benzene (6:1) to give yellow needles (3 g), m.p. 162—163°. Analytical details are given in Table 4. Variation in the ratio of hexane to benzene was necessary in some cases to effect crystallis-

TABLE 5

N-Sulphenylimines $R^1R^2C{=}NSR^3$ *

Compound	R^1	R^2	R^3	Yield (%)	M.p. (°C)	Calc. (%) C	Calc. (%) H	Calc. (%) N	Found (%) C	Found (%) H	Found (%) N
(1) [b]	H	H	$2\text{-}NO_2C_6H_4$	33	211—213	46.2	3.3	15.4	[a]		
(2) [c]	CH_3	CH_3	$2,4\text{-}(NO_2)_2C_6H_3$	37	154—156	42.4	3.5	16.5	42.5	3.5	16.5
(3) [b]	Pr^i	Pr^i	$2,4\text{-}(NO_2)_2C_6H_3$	6	145—150	50.2	5.5	13.5	50.2	5.5	13.8
(4) [b]	$C_6H_5CH_2$	$C_6H_5CH_2$	$2\text{-}NO_2C_6H_4$	56	97—98	69.6	5.0	7.7	69.4	4.7	7.3
(5) [b]	$C_6H_5CH_2$	$C_6H_5CH_2$	$2,4\text{-}(NO_2)_2C_6H_3$	93	130—131	61.9	4.2	10.3	62.3	4.4	10.2
(6)	$4\text{-}CH_3C_6H_4$	$4\text{-}CH_3C_6H_4$	$4\text{-}NO_2C_6H_4$	66	144—144.5	69.6	5.0	7.7	69.5	4.9	7.8
(7)	$4\text{-}CH_3C_6H_4$	$4\text{-}CH_3C_6H_4$	$4\text{-}ClC_6H_4$	56	97—98	71.7	5.1	4.0	72.0	5.4	4.0
(8)	$4\text{-}CH_3C_6H_4$	$4\text{-}CH_3C_6H_4$	C_6H_5	57	77.5—78.5	79.5	6.0	4.4	79.9	4.4	4.3
(9)	$4\text{-}CH_3C_6H_4$	$4\text{-}CH_3C_6H_4$	$4\text{-}CH_3C_6H_4$	40	127—128.5	79.7	6.4	4.2	79.7	6.5	4.1
(10)	$4\text{-}CH_3C_6H_4$	$4\text{-}CH_3C_6H_4$	$4\text{-}CH_3OC_6H_4$	55	89—90	76.1	6.1	4.0	76.2	5.9	3.9
(11)	$4\text{-}CH_3C_6H_4$	$4\text{-}CH_3C_6H_4$	$2,4\text{-}(NO_2)_2C_6H_3$	59	234—235.5	61.9	4.2	10.3	61.6	4.2	10.4
(12)	$4\text{-}CH_3C_6H_4$	$4\text{-}CH_4C_6H_4$	$4\text{-}Cl\text{-}2\text{-}NO_2C_6H_3$	25	171—172	63.6	4.3	7.1	63.7	4.4	6.9
(13)	$4\text{-}CH_3C_6H_4$	$4\text{-}CH_3C_6H_4$	$2\text{-}NO_2C_6H_4$	65	151—152	69.6	5.0	7.7	69.6	4.7	8.1
(14)	$4\text{-}CH_3C_6H_4$	$4\text{-}CH_3C_6H_4$	$4\text{-}CH_3\text{-}2\text{-}NO_2C_6H_3$	61	147—147.5	70.2	5.4	7.4	70.1	5.4	7.3
(15)	$4\text{-}CH_3C_6H_4$	$4\text{-}CH_3C_6H_4$	$4\text{-}CH_3O\text{-}2\text{-}NO_2C_6H_3$	26	134—138	67.3	5.1	7.1	67.4	5.1	6.9
(16)	$4\text{-}CH_3C_6H_4$	$4\text{-}CH_3C_6H_4$	Cl_3C	54	123—124	53.6	3.9	3.9	54.1	3.9	4.0
(17)	$4\text{-}CH_3C_6H_4$	$4\text{-}CH_3C_6H_4$	$(C_6H_5)_3C$	56	204—204.5	84.4	6.0	2.9	84.4	6.2	2.65
(18)	$4\text{-}CH_3C_6H_4$	$4\text{-}CH_3C_6H_4$	$C_6H_5CH_2$	60	112.5—114	79.7	6.4	4.2	80.1	6.8	4.0
(19)	$4\text{-}CH_3C_6H_4$	$4\text{-}CH_3C_6H_4$	CH_3	65	74—75	75.3	6.7	5.5	75.0	6.6	5.2
(20)	$4\text{-}CH_3C_6H_4$	$4\text{-}CH_3C_6H_4$	$(CH_3)_3C$	32	78—79	76.7	7.8	4.7	76.7	8.05	4.65
(21)	$4\text{-}CH_3C_6H_4$	$4\text{-}CH_3C_6H_4$	$(4\text{-}CH_3C_6H_4)_2C{=}N$	78	233—224.5	80.3	6.3	6.3	80.2	6.3	6.1
(22)	$ClCH_2$	$ClCH_2$	$2\text{-}NO_2C_6H_4$	60	59—60	38.7	2.9	10.0	39.2	2.9	10.1
(23)	CF_3	CF_3	$2\text{-}NO_2C_6H_4$	41	42.5—43	33.9	1.3	8.8	[a]		
(24)	CF_3	CF_3	C_6H_5	22	b.p. 45—55 at 0.05 mmHg	39.6	1.8	5.1	[a]		
(25)	C_6H_5	$4\text{-}CH_3C_6H_4$	$2,4\text{-}(NO_2)_2C_6H_3$	56	244—245	61.1	3.8	10.7	61.4	3.8	10.5
(26)	C_6H_5	$4\text{-}CH_3C_6H_4$	$4\text{-}Cl,2\text{-}NO_2C_6H_3$	50	153—154	62.7	3.9	7.4	62.9	4.1	7.0
(27)	C_6H_5	$4\text{-}CH_3C_6H_4$	$2\text{-}NO_2C_6H_4$	49	121—121.5	69.0	4.6	8.0	69.3	4.8	7.9

* Compounds prepared by method 2 except where otherwise stated.

[a] Analysed by mass spectral molecular weight determination. Compound (1) (Found: *m/e* 182.014846. Required: *M*, 182.014996); compound (24) (Found: *m/e*, 317.989391. Required: *M*, 317.98969); compound (24) (Found: *m/e*, 273.005681. Required: *M*, 273.005631). [b] Prepared by method 1a. [c] Prepared by method 1.

ation, and ethanol was used as an alternative to this solvent.

The *N*-sulphenylimine derived from 2,2,2-trifluoro-1-trifluoromethylethylidineamine and benzenesulphenyl chloride was an oil, which was purified by fractional distillation, and characterised by the n.m.r. and mass spectra.

Elemental analyses for these compounds are given in Table 5 and the corresponding ^1H n.m.r. spectra in Table 6.

N.m.r. Procedures.—(a) *Symmetrical* N-*sulphenylimines.* In a particular experiment, the compound (0.08 g) was dissolved in deuteriochloroform (0.4 ml) and transferred to a dry n.m.r. tube (4.7 mm diam.). Spectra were obtained generally with a 60 MHz Perkin-Elmer R10 spectrometer,* equipped with a variable temperature probe. The temperature was measured by a copper–constantan thermocouple situation close to the sample tube, attached to a Pye portable potentiometer (7569P).

Each spectrum was obtained with both forward and reverse scanning, usually at a sweep width of 1 Hz per division and a sweep rate of 32 Hz per min. For 20% solutions the field strength was set at 500 or 630 μV to avoid saturation effects. For experiments to determine the free energy only, spectra were obtained at *ca.* 2 °C intervals around the coalescence point. To obtain the maximum peak separation in the absence of exchange it was necessary to record spectra in the temperature range 30—40° below the coalescence point, or until the separation became constant.

(b) *Unsymmetrical* N-*sulphenylimines.* A saturated solution of one form of an unsymmetrical thio-oxime ether at −60° was transferred to the probe maintained at a suitable temperature. Spectra of the methyl group of *p*-tolyl (δ 2.4) were obtained initially and at accurately noted intervals over 2 h at −32, −30, −26, and −22°. Relative concentrations of the isomers were determined for each scan using the integrated peak areas obtained by cutting out duplicate photocopies of the spectra and weighing them. Since the peaks overlapped marginally, it was necessary to extrapolate each peak to zero absorption.

* When the chemical shift differences between isomers was too small, a 100 MHz spectrometer (Varian HA100) was used.

APPENDIX

The extended Hückel formalism has been given by several workers,[24,25] but the treatment has not been widely used. Apart from the original work of Salem [25] on [2 + 2] and [2 + 4] cycloadditions, other applications have been qualitative, *e.g.* the conformation of simple molecules,[48] the anomeric effect,[31] and the variable electronic effect of alkyl groups on acid dissociation,[49] Recently, Wolfe *et al.* have used this method within an SCF framework for the conformation of propene and similar systems.[50]

The appropriate equations for a two- and four-electron interaction are (7) and (8) where C_{rj} and C_{sk} are coefficients

$$\Delta E^{(2)} = \frac{2C_{rj}^2C_{sk}^2(H_{jj} - E_iS_{ij})^2}{E_i - E_j} \quad (7)$$

$$\Delta E^{(4)} = -2C_{rj}^2C_{sk}^2[2H_{ij}S_{ij} - (E_i + E_j)S_{ij}^2] \quad (8)$$

on atoms r and s for orbitals j and k respectively, H_{ij} is the Hamiltonian, S_{ij} the two-centre overlap integral, and E_i and E_j are the corresponding energies of the interacting orbitals.

By making the usual assumption (9), equation (8)

$$H_{ij} = 0.5\,k(E_i + E_j)S_{ij} \quad (9)$$

simplifies to (10) which was used in the estimation of

$$AE^{(4)} = -2(k - 1)(E_i + E_j)S_{ij}^2 \quad (10)$$

TABLE 6

Details of n.m.r. absorbances at probe temperature (33.4 °C)

Compound	Chemical shift δ
(1)	4.5 (s, 2 H, CH_2), 7.1—8.3 (m, 4 H, ArH)
(2)	2.2 (s, 6 H, 2 × CH_3), 8.2—9.1 (m, 3 H, ArH)
(3)	1.2—1.3 (q, 12 H, 4 × CH_3), 2.5—3.5 (m, 2 H, 2 × CH), 8.2—9.1 (m, 3 H, ArH)
(4)	3.7—4.0 (d, 4 H, 2 × CH_2), 7.0—8.5 (m, 14 H, ArH)
(5)	3.5—3.7 (d, 4 H, 2 × CH_2), 7.0—8.8 (m, 13 H, ArH)
(6)	2.3—2.4 (d, 6 H, 2 × CH_3), 6.2—8.0 (m, 12 H, ArH)
(7)	2.3—2.4 (d, 6 H, 2 × CH_3), 6.6—7.9 (m, 12 H, ArH)
(8)	2.3—2.4 (d, 6 H, 2 × CH_3), 7.0—7.9 (m, 13 H, ArH)
(9)	2.2—2.4 (t, 9 H, 3 × CH_3), 7.0—8.0 (m, 12 H, ArH)
(10)	2.3—2.4 (d, 6 H, 2 × CH_3), 3.75 (s, 3 H, OCH_3), 6.8—7.8 (m, 12 H, ArH)
(11)	2.3—2.4 (d, 6 H, 2 × CH_3), 7.1—9.1 (m, 11 H, ArH)
(12)	2.3—2.4 (d, 6 H, 2 × CH_3), 7.0—8.8 (m, 11 H, ArH)
(13)	2.3—2.4 (d, 6 H, 2 × CH_3), 7.0—8.8 (m, 12 H, ArH)
(14)	2.3—2.4 (t, 9 H, 3 × CH_3), 7.0—8.8 (m, 11 H, ArH)
(15)	2.3—2.4 (d, 6 H, 2 × CH_3), 3.85 (s, 3 H, OCH_3), 7.0—8.8 (m, 11 H, ArH)
(16)	2.35 (s, 6 H, 2 × CH_3), 7.0—7.6 (m, 8 H, ArH)
(17)	2.35 (s, 6 H, 2 × CH_3), 7.0—7.5 (m, 23 H, ArH)
(18)	2.3—2.4 (d, 6 H, 2 × CH_3), 4.3 (s, 2 H), 7.0—7.6 (m, 13 H, ArH)
(19)	2.3—2.4 (d, H, 2 × CH_3), 2.7 (s, 3 H, CH_3), 7.0—7.5 (m, 8 H, ArH)
(20)	1.45 (s, 9 H, 3 × CH_3), 2.3—2.4 (d, 6 H, 2 × CH_3), 7.0—7.6 (m, 8 H, ArH)
(21)	2.3—2.4 (d, 12 H, 4 × CH_3), 7.0—7.5 (m, 16 H, ArH)
(22)	4.95 (s, 4 H, 2 × CH_2), 7.2—8.6 (m, 4 H, ArH)
(23) [a]	7.2—8.6 (m, ArH)
(24) [b]	7.2—8.8 (m, ArH)
(25)	2.3—2.4 (d, 3 H, CH_3), 7.1—9.1 (m, 12 H, ArH)
(26)	2.3—2.4 (d, 3 H, CH_3), 7.1—8.8 (m, 12 H, ArH)
(27)	2.3—2.4 (d, 3 H, CH_3), 7.1—8.8 (m, 13 H, ArH)

[a] ^{19}F N.m.r.: +69.0 p.p.m. from $CFCl_3$ (S, 2 × CF_3). [b] ^{19}F N.m.r.: +69.8 p.p.m. from $CFCl_3$ (s, 2 × CF_3)

repulsion energies on page 431, with k 1.75 and $E_i \simeq E_j \simeq -12$ eV.

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