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BARRIERS TO TOPOMERIZATION* IN IMINODITHIOCARBONATES
A HAMMETT CORRELATION AND COMPLETE LINESHAPE STUDY

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Abstract—The rate of topomerization at the C=N bond in a series of *p*-substituted dimethyl N-phenyliminodithiocarbonates has been studied by the NMR technique at the coalescence temperature. For the *p*-methoxy compound the rate has been measured over a larger temperature interval by the complete lineshape method, and the enthalpy and entropy of activation have been found to be 11·8 ± 0·4 kcal/mole and − 11·1 ± 1·7 e.u. The entropy of activation is more negative than expected for an inversion path, whereas the low reaction constant in the Hammett correlation supports this mechanism.

Two mechanisms have been considered for the isomerization of azomethines and related compounds with C=N double bonds, *viz* the inversion and the rotation paths. In the former, often referred to as "the lateral shift mechanism", the substituent on nitrogen moves in the plane of the molecule, and in the linear transition state the N atom is sp-hybridized. In the rotational alternative the C—N π bond is broken either homolytically or heterolytically. Lehn and Munsch[1] have performed *ab initio* calculations on the two alternative paths for methylenimine and found a barrier of 27·9 kcal/mole for inversion and 57·5 kcal/mole for rotation. However, it seems *a priori* quite possible that substituents on the imino C atom, which can stabilize a positive charge and/or substituents on the N atom, which can stabilize a negative charge, should facilitate the heterolytic rotational path to such an extent as to make it the more facile one. Furthermore, a mixed inversion–rotation mechanism is conceivable, as has been pointed out by several authors.[2]

The rotation path has been advocated by Marullo and Wagener,[3, 2c] who stress that the C=N barriers decrease strongly with increasing conjugating capacity of the substituents on the imino C atom. Curtin *et al.*[2a] on the other hand contend that the low barriers in many imines compared with the simple olefins necessitate a different mechanism for the C=N isomerization. This argument, however, has lost some of its validity since push–pull substituents have been shown to lower the C=C barrier to values in the region 15–25 kcal/mole[4] and even lower.[5]

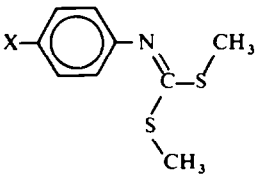
Stronger arguments in favour of the inversion mechanism have been obtained by the demonstration that *ortho*-substituents in the N-phenyl ring accelerate the iso-

* This term has been proposed by H. Kessler, *Angew. Chem.* **82**, 237 (1970), International Edition **9**, 219, for degenerate isomerizations.

merization of N-phenyl-ketimines,[6] quinone anils,[7] and N-phenyl-N′,N′,N″,N″-tetramethylguanidines.[8] Recently, Kessler and Leibfritz[9] have given a further, very elegant proof for the total dominance of the inversion mechanism in N-(*o,o′*- di*iso*propylphenyl)-quinonimines, -iminocarbonates, -iminodithiocarbonates, and -guanidines. In these compounds the exchange of the diastereotopic Me groups in the isopropyl groups occurs with the same rate as the topomerization at the C=N bond, which would not have been the case if a rotation or mixed inversion–rotation mechanism had applied.

Quite recently, Raban[10] has reported the results of CNDO/2 calculations on methylenimine, hydroxymethylenimine, and guanidine, which form a series with increasing electron-donating capacity of the substituents on the imino C atom. The calculated barriers to inversion and rotation in methylenimine, 31·1 and 61·1 kcal/mole respectively, agree well with those given in Ref 1. The corresponding values for hydroxymethylenimine are 31·8 and 50·7 kcal/mole, and for guanidine 36·1 and 28·4 kcal/mole, i.e. in the latter case the rotational mechanism should be favoured. However, the results of Raban and Kessler need not be incompatible, since for steric reasons the dimethylamino groups in N,N,N′,N′-tetramethylguanidines cannot be coplanar and cannot develop electron-donating capacity equivalent to that of the amino groups in guanidine. Furthermore, the presence of an aryl group bonded to the imino N atom and nearly orthogonal to the $N{=}CN_2$ system may stabilize the transition state to inversion by interaction between the π-orbitals of the aromatic ring and the lone pair on the imino N atom.

We have hoped to contribute to the elucidation of the mechanism by measuring the entropy of activation for the isomerization at the C=N bond in a suitable compound, and we also hoped to obtain useful information from a Hammett correlation in a series of *para*-substituted analogs. Dimethyl N-phenyliminodithiocarbonates (**1A–1H**) have been chosen as compounds with suitable intermediate electron-donating capacity of the substituents on the imino C atom. The free energy of activation for the isomerization of **1D** has been reported previously,[11] and the result is in reasonable agreement with the one obtained in the present work (Table 5).



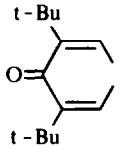
1

	X
A	$(CH_3)_2N$
B	CH_3O
C	CH_3
D	H
E	F
F	CH_3OCO
G	CN
H	NO_2

DISCUSSION

Hammett correlation. The reaction constant ρ in the Hammett equation[12] has been a useful tool for the elucidation of reaction mechanisms, since it constitutes a probe for the electronic requirements of the reaction centre. From the $\Delta G^{\ddagger}$ values at the

TABLE 1. Hammett reaction constants for the isomerization at the C=Z bond in p-RC_6H_4Z=CXY (at 300 K unless otherwise stated)

	X	Y	Z	$\rho(\sigma_p)$	R^a	$\rho(\sigma^-)$	R	Reference
(1)	MeS	MeS	N	1·13[b] 1·11[c]	0·940 0·980	0·84[b] 0·81[c]	0·957 0·980	This work
(2)	Me_2N	Me_2N	C—CN	3·33	0·990	1·95	0·991	15
(3)	Ph	H	N	2·01	0·89	2·01[d]	0·89	17
(4)	p-$MeOC_6H_4$	p-$MeOC_6H_4$	N	2·22	1·00	1·72	0·99	2a
(5)	Me_2N	Me_2N	N	—	—	2·21	0·98	8
(6)			N	—	—	1·5 ± 0·3[e]	—	7b
(7)	MeO	MeO	N	2·15	0·96	1·43	0·98	18

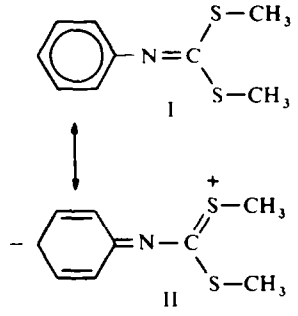
a Regression coefficient
b With **1E**
c Without **1E**
d Only +M substituents
e At 100°

coalescence temperature we have calculated the rate constants at 300 K. assuming the same $\Delta S^{\ddagger}$ (i.e. −11 e.u., Table 4) for all compounds **1**. The log k values give about equally good correlations with σ_p and σ^- (both from Ref 13) (Table 1). The largest deviation from the regression line is shown by the p-fluoro compound (**1E**). The other compounds with +M substituents also show some scatter, and it is of interest to note that log k is not larger for the p-MeO than for the p-dimethylamino compound, an anomaly also observed by Rieker and Kessler for the corresponding quinone anils.[14]

Both for the rotation and for the inversion mechanism a positive ρ-value is to be expected. In the transition state for rotation, the π-electrons of the C=N bond should be transferred to the N atom, and the reaction should be facilitated by substituents on the N-Ph group, which can assist in the stabilization of a negative charge. Kessler has studied the rotations around the C=C, the C—aryl, and both C—N bonds in a series of *para*-substituted 1,1-bis(dimethylamino)-2-cyano-2-phenylethylenes.[15] He reports $\Delta G^{\ddagger}$ at the coalescence and different ρ-values resulting from correlations with σ^- depending on different assumed $\Delta S^{\ddagger}$ values. $\Delta S^{\ddagger}$ for the rotation around the C=C bond in the p-unsubstituted compound (**11**) has been found by a complete lineshape study to be $-6{\cdot}6 \pm 0{\cdot}4$ e.u.[16] Using this value and the $\Delta G^{\ddagger}$ values given in Ref 15 we have calculated the ρ-values found in Table 1. Evidently the ρ-values for the true rotation are higher than those found in the present work, though the two systems are so different that not too much weight can be laid on the comparison.

The transition state for inversion can also be expected to be stabilized by electron-attracting *para*-substituents. If the phenyl ring in the iminodithiocarbonates is twisted out of the molecular plane in the transition state, its π-orbitals will overlap with the lone pair on nitrogen in its p-orbital to an extent that is determined by the angle of twist. This interaction stabilizes the transition state,[8a] and the stabilization

will be increased by $-M$ substituents in the *para*-position. In a planar transition state, a resonance interaction, visualized by I ⇔ II can be anticipated. This applies also to the initial state, but it should be more important in the transition state because the sp-hybridized N atom should give shorter C—N bonds. The actual stabilization will be composed of both these effects, and their contributions will be determined by the angle of twist around the N—aryl bond. In all events a positive ρ-value is expected, though smaller than for the rotation. The calculations of Raban[10] give much larger dipole moments for the transition states for rotation than for those for inversion.



In Table 1 a selection of ρ-values for isomerizations at C=N bonds in different types of anils has been collected from the literature. When possible the values have been recalculated to T = 300 K, with correlation against σ_p and σ^-, and assuming $\Delta S^{\ddagger} = 0$. For compounds **5**, **6**, and **7** the inversion mechanism has been demonstrated by the steric acceleration and magnetic non-equivalence methods,[9] and it is likely to apply also to **3** and **4** since steric acceleration has been demonstrated also for simple N-arylketimines.[6] The ρ-values show a considerable spread, and the high value for **5** is unexpected. It may be due to a relatively large importance of the polar form corresponding to II, but it appears as if the ρ-value gives no clear mechanistic distinction in the present case. Still, the value found for the iminodithiocarbonates is the lowest in all N-arylimines studied so far, and it indicates that the isomerization follows the inversion path.

Activation entropy. This parameter can be expected to differ considerably for inversions and rotations in the same system. In the initial state the molecule is slightly polar, due to the electron attraction of the imino N atom, and somewhat orientated solvation should occur due to dipole-induced dipole interactions. In the transition state for inversion the solute dipole moment is probably considerably decreased since the nitrogen lone pair is transferred from an sp^2 to a p orbital. The two C—N bond dipoles are doubtlessly increased due to the change in N hybridization, but they are antiparallel and mutually compensating in the transition state, whereas they are at an angle in the initial state*. This effect might be somewhat counteracted by an increased weight of limiting structures of type II, but a decrease in polarity and thus in order in the solvent cage is likely, which should give a positive contribution to $\Delta S^{\ddagger}$. A similar situation arises in amides, which suffer a loss in polarity in the transition state. Reliable $\Delta S^{\ddagger}$ values from complete lineshape studies are now available for

* We are grateful to the referee for pointing this out to us.

formamide ($+2{\cdot}7 \pm 0{\cdot}6$ e.u. in 2-pentanone[19]) and N,N-dimethyltrichloroacetamide ($+0{\cdot}3 \pm 2{\cdot}3$ e.u., neat[20]. Also Raban *et al.*[2b] found $\Delta S^{\ddagger} = -2$ e.u. for an N-benzenesulphonylketimine by a combination of NMR equilibration and lineshape methods, and Curtin *et al.*[2a] obtained $\Delta S^{\ddagger} = 2{\cdot}1 \pm 1{\cdot}5$ e.u. from a UV study of the equilibration of an unsymmetrical benzophenone ketimine.

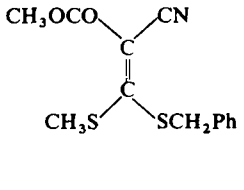
As shown by Raban,[10] the dipole moment of the transition state to rotation is larger than that of the initial state, though the polarization of the π-bond is partly compensated by overlap of the imino nitrogen lone pair with the *p*-orbital on the imino C atom. The order in the solvent cage should be increased in the transition state, and a negative contribution to $\Delta S^{\ddagger}$ should result. Some $\Delta S^{\ddagger}$ values for true rotations that have been determined by complete lineshape or NMR equilibration studies are shown in Table 2.

TABLE 2

Compound	**1B**	**8**	**9**	**10**	**11**
$\Delta S^{\ddagger}$ e.u.	$-11{\cdot}1 \pm 1{\cdot}7$	-24 ± 3[21]	$-17{\cdot}3 \pm 1{\cdot}4$[21]	$-3{\cdot}2 \pm 3$[22]	$-6{\cdot}6 \pm 0{\cdot}4$[16]

The $\Delta S^{\ddagger}$ value obtained from the complete lineshape treatment of **1B**, $-11{\cdot}1 \pm 1{\cdot}7$ e.u., is more negative than expected for an inversion, and it should fit better into a rotation or a mixed inversion–rotation mechanism.

However, more data seem to be required concerning the detailed mechanism of solvation of iminodithiocarbonates in aromatic solvents, before a safe conclusion can be drawn regarding the $\Delta S^{\ddagger}$ values to be expected for the two kinds of mechanism.



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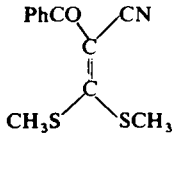

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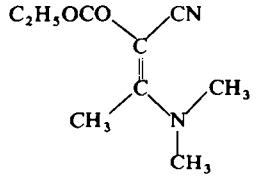

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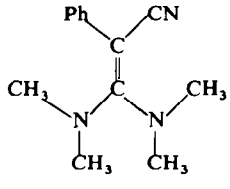
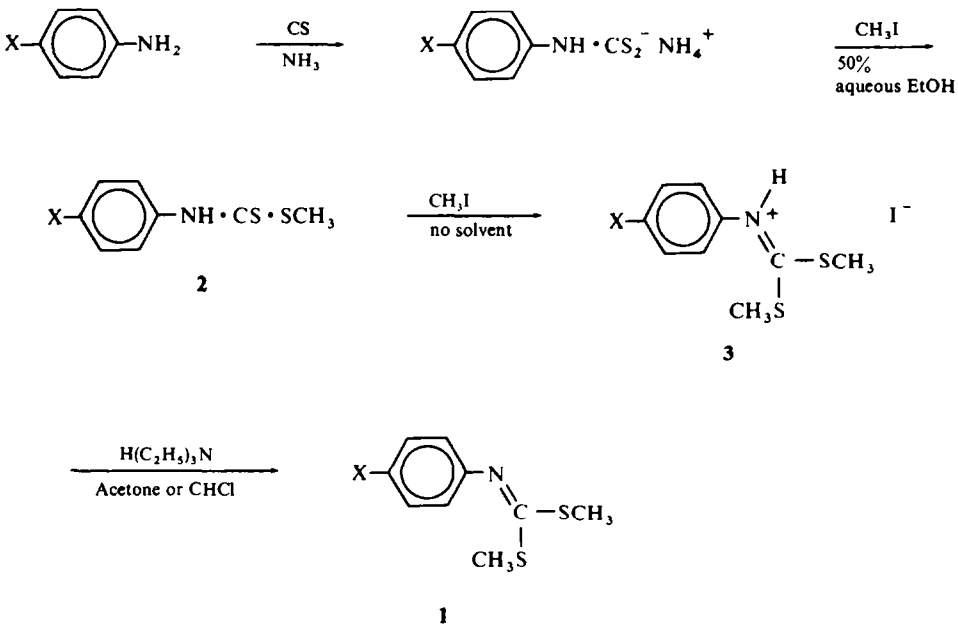


11

EXPERIMENTAL

Preparations. Compounds **1A–1E** were prepared by reaction between the appropriate amine, CS_2, and ammonia to give the ammonium dithiocarbamates.[23] These were dimethylated in two steps to the immonium salts **3**, which were deprotonated to give **1**.



The dithiocarbamate **2A** gave the *p*-trimethylammonium analog on reaction with MeI, and **1A** was instead prepared by deprotonation of **2A** with NaOEt followed by methylation with MeI.

The iminodithiocarbonates with electron-withdrawing substituents (**1F–1H**) could not be prepared by the above process since the amines did not react with CS_2 and ammonia. Instead, the amines were treated with NaH in hexamethylphosphortriamide to give the amine anions, which reacted readily with CS_2. The resulting dithiocarbamates were dimethylated with Me_2SO_4 and deprotonates with NaH in one operation. The products were precipitated by the addition of water to the reaction mixture and purified by recrystallization.

Compounds **1C** and **1D** have been described previously.[24] M.ps, b.ps and elemental analyses for the new compounds **1** are found in Table 3.

The methyl dithiocarbamates **2A** and **2E** do not seem to have been described previously. Their data are also found in Table 3. The preparation of compounds **2B–2D** is described in references.[25–27]

TABLE 3

Compound	B.p. or m.p. °C	Calc. C	H	N	S	Found C	H	N	S	Solvent for recrystallization
1A, $C_{11}H_{16}N_2S_2$	106–107	55·0	6·71	11·7	26·7	54·8	6·67	11·5	26·7	*n*-propanol
1B, $C_{10}H_{13}NOS_2$	160–162 2 mm Hg	52·8	5·76	6·16	28·2	52·7	5·78	6·16	28·4	
1E, $C_9H_{10}FNS_2$	148–150 6 mm Hg	50·2	4·68	6·51	29·8	50·7	5·08	6·60	29·5	
1F, $C_{11}H_{13}NO_2S_2$	79– 80	51·7	5·13	5·49	25·1	52·0	5·17	5·56	25·1	ligroin (60–100°)
1G, $C_{10}H_{10}N_2S_2$	82– 84	54·0	4·53	12·6	28·8	54·3	4·64	12·9	28·6	ligroin (60–100°)
1H, $C_9H_{10}N_2O_2S_2$	66– 67	44·6	4·16	11·6	26·5	44·8	4·02	11·5	25·9	methanol
2A, $C_{10}H_{14}N_2S_2$	130–134	53·1	6·23	12·4	28·3	53·1	6·32	12·4	28·2	chloroform
2E, $C_8H_8FNS_2$	108–109	47·7	4·01	6·96	31·9	48·0	4·50	7·61	32·0	chloroform + ligroin

TABLE 4. Results from a complete lineshape treatment of **1B** in fluorobenzene

TK	$\Delta\nu_0$ Hz	T_2 sec.	τ sec.	$\Delta G^{\ddagger}$ kcal/mole
268·9	11·0	0·318	0·0956	14·8
270·8	11·1	0·354	0·0697	14·7
274·1	11·3	0·318	0·0519	14·8
276·4	11·2	0·318	0·0442	14·8
278·4	10·9	0·318	0·0400	14·9
282·5	10·6	0·290	0·0338	15·0
285·5	10·3	0·318	0·0239	15·0
288·1	10·3	0·580	0·0195	15·0
291·1	10·3	0·374	0·0151	15·0
292·4	10·3	0·304	0·0140	15·0
293·0	10·3	0·640	0·0130	15·0
295·0	10·3	0·460	0·0113	15·0

$\Delta H^{\ddagger} = 11{\cdot}8 \pm 0{\cdot}4$ kcal/mole
$\Delta S^{\ddagger} = -11{\cdot}1 \pm 1{\cdot}7$ e.u.
The errors are standard deviations from the least squares plot.

NMR spectra and evaluation of rate constants. The non-exchanging chemical shifts between the S-Me signals, $\Delta\nu_0$, are quite small in the common non-aromatic solvents (see Ref 11), but they increase in aromatic solvents, and we have chosen fluorobenzene, though for solubility reasons **1G** had to be measured in a 3:1 mixture of fluorobenzene and $CDCl_3$. The spectra were recorded with a Varian Model HA-100 NMR spectrometer, using frequency sweep with the internal lock on the TMS signal. The temps were measured as previously described.[28] Compound **1B** was studied at 12 different temps, and at each temp at least three spectra were automatically digitalized and transferred to a punched tape. In each spectrum the intensity was recorded at about 125 different frequencies. The transverse relaxation times were determined by monitoring the line width, W'_{ref}, of the OMe signal at each temp, and the line width of a methylthio signal, W_1, at a temp below the region where exchange broadening is noticeable. At this temp the line width of the reference signal is W_{ref}, and T_2 at each temp is obtained from formula (1), which is derived under

$$T_2 = \frac{1}{\pi(W_1 + W'_{ref} - W_{ref})} \tag{1}$$

TABLE 5. Coalescence data for compounds **1**, in fluorobenzene unless otherwise stated

Compound	X	$\Delta\nu_0$ Hz	T_c K	$\Delta G^{\ddagger}_{300}$ kcal/mole	(from Ref. 13) σ_p	σ^-
1A	$(CH_3)_2N$	14·8	286·3	15·0	−0·60	
1B	CH_3O	14·8	283·0	15·0	−0·27	
1B[a]	CH_3O	2·1	270·9	15·0	−0·27	
1C	CH_3	14·3	277·0	14·6	−0·17	
1D	H	14·0	270·7	14·3[b], 14·0[c]	0	
1E	F	14·6	280·0	14·8	0·06	
1F	CH_3OCO	12·9	247·9	13·5	0·48	0·64
1G[d]	CN	12·6	235·6	13·3	0·63	1·00
1H	NO_2	12·3	232·3	13·1	0·78	1·27

a In $CDCl_3$
b Ref. 11 gives $13{\cdot}7 \pm 0{\cdot}3$ kcal/mole (at coalescense)
c At coalescence
d In 75% C_6H_5F + 25% $CDCl_3$

the assumption that the line widths of both signals are equally affected by homogeneity and viscosity changes. The punched tapes were fed to a Univac 1108 computer together with values of T_2 and coarse estimates of the mean lifetime τ and $\Delta\nu_0$. The best values for the two latter parameters were found by a least squares fitting of lineshapes, calculated by the McConnell equation[29a], to the experimental spectra, using the Stepit procedure.[29b] From the $\Delta\nu_0$ values below coalescence, suitable values for the higher temps were estimated, since above coalescence $\Delta\nu_0$ and τ are covariant. From the τ values the activation parameters were obtained by plotting $\log 1/2\tau T$ against $1/T$ according to the Eyring equation in the form (2).

$$\log\frac{1}{2\tau T} = -\frac{\Delta H^{\ddagger}\log e}{RT} + \frac{\Delta S^{\ddagger}\log e}{R} + \log\frac{k_B}{h} \tag{2}$$

The parameters for **1B** are found in Table 4. Compounds **1A** and **1C–1H** have only been studied at the coalescence temp, employing the expression (3).[30] The results are presented in Table 5.

$$\tau = \frac{1}{\pi\Delta\nu\sqrt{2}} \tag{3}$$

The $\Delta G^{\ddagger}$ value found for **1B** at the coalescence temperature agrees very well with the one found by the complete line-shape method at the same temperature.

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