

## Studies of Polarised Ethylenes

### Part I. Barriers to Rotation Around the Carbon-Carbon Double Bond in 1,1-Bis-alkylthio-ethylenes

J. SANDSTRÖM and I. WENNERBECK

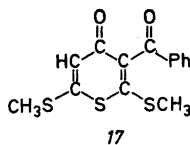
*Division of Organic Chemistry, Chemical Center, University of Lund, S-220 07 Lund 7, Sweden*

The free energies of activation for rotation around the  $C_1-C_2$  bond in ethylenes with alkylthio groups on  $C_1$  and electron-attracting groups on  $C_2$ , have been determined by the NMR technique at the coalescence temperature. In two cases the kinetics have been studied over a larger temperature interval. The large negative activation entropies are in agreement with a polar transition state. The  $\Delta G^\ddagger$  values do not correlate with the Hammett  $\sigma_p$  values of the electron attracting substituents, but reasonable correlations are obtained with  $\pi$ -bond orders and  $\pi$ -electron energy changes calculated by simple molecular orbital methods. Infrared spectra indicate a considerable polarisation of the  $C_1-C_2$  bonds, but, according to the calculated bond orders, the double bond character is essentially preserved.

The energy barriers separating *cis* and *trans* forms of simple ethylenes, such as 1,2-dideuteroethylene<sup>1</sup> and 2-butene,<sup>2</sup> are as high as 60–65 kcal/mole, but they are substantially lower in ethylenes carrying substituents with a push-pull effect. Thus Calvin and Alter<sup>3</sup> found an  $E_a$  value of 17.1 kcal/mole for the *cis* to *trans* conversion of *p*-amino-*p'*-nitrostilbene ( $\Delta G^\ddagger = 30$  kcal/mole at 100°C) by light absorption measurements, and Shvo *et al.*<sup>4</sup> have measured considerably lower carbon-carbon double bond barriers in diacyl-enamines by NMR technique. Quite recently, Downing *et al.*<sup>5</sup> have published an extensive survey of the temperature dependent NMR spectra of 6-dimethyl-aminofulvenes, and in these compounds barriers to rotation around formal double bonds as low as 15.5 kcal/mole have been recorded.

We have investigated barriers to internal rotation and other physical properties in a large number of polarised ethylenes (for preliminary communications see Refs. 6, 7) hoping to find correlations between the structures of the compounds and the measured properties. We report here the results of a study of the barriers to rotation around the  $C_1-C_2$  double bonds in a number of





Compounds 2, 4, 5, 6, 7, and 16 have previously been described by Gompper and Töpfl,<sup>8</sup> compounds 2, 6, and 16 also by Söderbäck<sup>13</sup> and by Jensen and Henriksen.<sup>13</sup> Compound 12 has been prepared by Laakso<sup>14</sup> by hydrolysis of the ethyl ester analog of 15, and by Thuillier and Vialle<sup>15</sup> by direct reaction between acetone and carbon disulphide in the presence of potassium *tert.* amylate, followed by methylation. In the present work it was formed in the reaction between 2,4-pentanedione and carbon disulphide in ethanolic sodium ethoxide, and it was found identical with a product prepared essentially according to Ref. 15.

*1,1-Bis-methylthio-2-cyano-2-p-nitrophenylethylene (1).* *p*-Nitrophenylacetonitrile (0.2 mole) in dry benzene (200 ml) was added to a suspension of sodium hydride (0.4 mole) in dry benzene (150 ml). On addition of carbon disulphide (0.2 mole) to the cooled mixture no reaction was evident, but on addition of DMF (150 ml) the solution turned dark-green and the remaining sodium hydride was consumed. The reaction was completed by slight heating, and after cooling to 10°, methyl iodide (0.4 mole) was added. On the following day water was added, and the benzene layer was extracted with several portions of water to remove the remaining DMF. On evaporation of the benzene solution a dark green, semi-solid mass was obtained. Extraction several times with boiling ligroin (60–80°) gave yellow crystals (29.4 g, 55 % yield), m.p. 79–80°C. Further recrystallisations from ethanol did not change the m.p. [Found: C 49.9; H 3.97; N 10.2; S 24.0. C<sub>11</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub> (266.33) requires C 49.6; H 3.79; N 10.5; S 24.1].

*1-Benzylthio-1-methylthio-2-carbomethoxy-2-cyanoethylene (3).* Methyl cyanoacetate (0.1 mole) was added to a cooled solution of sodium methoxide (0.1 mole) in dry methanol (30 ml), followed by carbon disulphide (0.05 mole). The remaining carbon disulphide (0.05 mole) and sodium methoxide (0.1 mole) were added each in two portions with an interval of about 15 min. After 2 h methyl iodide (0.1 mole) was added, and after 1 h benzyl chloride (0.1 mole). On the following day the mixture was poured into water, the product extracted with ether, and after drying and evaporation it was brought to crystallisation by treatment with chloroform-petroleum ether at –80°C. The crude product (30 % yield) was recrystallised first from ethanol and then from toluene and gave colourless plates, m.p. 78–80°. [Found: C 56.9; H 4.81; N 4.81; S 22.7. C<sub>13</sub>H<sub>13</sub>NO<sub>2</sub>S<sub>2</sub> (279.38) requires C 55.9; H 4.69; N 5.01; S 23.0].

*1,1-Bis-methylthio-2-benzoyl-2-cyano-ethylene (8)* was prepared as 1, starting from benzoylacetonitrile.<sup>16</sup> The crude product (100 % yield) solidified spontaneously when the benzene solution was evaporated and it crystallised from a small volume of ethanol as pale yellow rods, m.p. 70–71°. [Found: C 57.8; H 4.67; N 5.23; S 25.3. C<sub>12</sub>H<sub>11</sub>NOS<sub>2</sub> (249.36) requires C 57.8; H 4.45; N 5.62; S 25.7].

*1,1-Bis-methylthio-2-benzoyl-2-ethoxycarbonylethylene (9)* was prepared as 1, starting from ethyl benzoylacetate. The crude product (60 % yield) crystallised from ethanol as colourless rods, m.p. 68–69°. [Found: C 56.5; H 5.46; S 21.5. C<sub>14</sub>H<sub>16</sub>O<sub>3</sub>S<sub>2</sub> (296.41) requires C 56.7; H 5.44; S 21.6].

*1,1-Bis-methylthio-2-acetyl-2-benzoylethylene (10)* was prepared as described for 1, starting from benzoylacetone and substituting HMP for DMF. When the crude product was recrystallised from methanol, the 4H-thiopyran-4-one 17, was obtained in 2 % yield as colourless prisms, m.p. 136–138°. [Found: C 54.6; H 3.90; S 30.9. C<sub>14</sub>H<sub>12</sub>S<sub>2</sub>O<sub>2</sub> (308.29) requires C 54.5; H 3.92; S 31.2].

When the mother liquor was evaporated and the residue recrystallised from a small amount of methanol, 10 was obtained in 13 % yield as pale yellow prisms, m.p. 57–59°. [Found: C 58.3; H 5.14; S 24.2. C<sub>13</sub>H<sub>14</sub>O<sub>2</sub>S<sub>2</sub> (266.38) requires C 58.6; H 5.29; S 24.1].

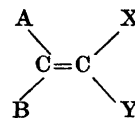
*1,1-Bis-methylsulphonyl-2-benzoyl-2-ethoxycarbonylethylene (11).* Hydrogen peroxide (30 %, 10 ml) and compound 9 (5.9 g) were refluxed in glacial acetic acid (65 ml) for 1.5 h. After evaporation the residue solidified and was recrystallised from 50 % aqueous

methanol to give colourless prisms (5.0 g, 70 % yield). A further recrystallisation from toluene gave colourless plates, m.p. 121–125° (decomp.). [Found: C 44.4; H 4.77; S 17.1.  $C_{14}H_{14}O_2S_2 \cdot H_2O$  (378.41) requires C 44.4; H 4.79; S 17.0].

*1,1-Bis-methylthio-2-acetyl-2-phenylethylene* (13) was prepared as described for 1, starting from phenylacetone. The semi-solid product was extracted several times with boiling ligroin (80–100°), and on cooling to –70° the combined ligroin solutions gave a yellow solid (35 % yield), which was recrystallised twice from ethanol to give colourless prisms, m.p. 45–46°C. [Found: C 59.6; H 5.95; S 26.8.  $C_{13}H_{14}OS_2$  (238.35) requires C 60.5; H 5.92; S 26.9].

*1,1-Bis-methylthio-2,2-diacetyl-ethylene* (14) was prepared as described for 1, starting from 2,4-pentanedione. The crude product (59 % yield) crystallised from methanol as colourless rectangular prisms, m.p. 59–60°C. [Found: C 47.1; H 5.92; S 31.1.  $C_8H_{12}O_4S_2$  (204.31) requires C 47.0; H 5.92; S 31.4].

*1,1-Bis-methylthio-2-acetyl-2-carbomethoxy-ethylene* (15) was prepared as described for 1, starting from methyl acetoacetate. The crude product (42 % yield) crystallised from light petroleum (20–40°) at low temperature as colourless prisms, m.p. 21–22°. [Found: C 43.3; H 5.48; S 29.1.  $C_8H_{12}O_4S_2$  (220.31) requires C 43.6; H 5.49; S 29.1].

Table 1. NMR parameters and  $\Delta G^\ddagger$  values for  in *o*-dichlorobenzene.

Compound	$\Delta\nu_0$ Hz	$T_c$ K	$\Delta G^\ddagger$ kcal/mole
1	18.5	> 470	> 25
2	8.5	462.3	24.8
4	10.0	451.2	24.0
5	6.0	455.1	24.7
7	20.5	> 470	> 25
8	17.0	397.9	20.6
9	18.4	375.4	19.4
10	22.2	352.9	18.0
11	3	> 470	> 25
12	4	> 470	> 25
13	10	> 470	> 25
15	0	unknown	unknown

*Barrier measurements.* Most of the barriers have been measured as free energies of activation,  $\Delta G^\ddagger$ , and only at the coalescence temperature (Table 1), utilising the simplified expression  $k = \pi \Delta\nu_0 / \sqrt{2}$ <sup>17</sup> and the Eyring equation. In order to study the temperature dependence of  $\Delta G^\ddagger$ , we measured the rate of rotation of 8 by the complete lineshape method over a temperature interval of about 30°C. The rate constants were evaluated by a computer program,<sup>18</sup> which varies the parameters and minimizes the sum of the squared deviations at given frequencies between calculated and experimental lineshapes by the STEPIT procedure.<sup>19</sup> The lineshape measurements were performed with *o*-dichlorobenzene as solvent, and the recording of the spectra and the temperature measurements were performed as described previously.<sup>20</sup>

However, the temperature dependent shift between the OH and CH<sub>2</sub> signals of the ethylene glycol capillary were calibrated with a copper constantan thermocouple, inserted in a spinning dummy tube at the depth of the receiver coil. The thermocouple was previously calibrated against a high-precision platinum resistance thermometer (Rosemount Model E 109). A good straight line was obtained, but the slope differed from that given by Varian. At +50°C, the temperature obtained by the Varian calibration curve was 1.5° too low, and at +190° it was 4.0° too low.

We have also measured the rate of *cis* to *trans* conversion of 3 by integration at 10°, 20°, 30°, and 40°C (Table 3). For solubility reasons these measurements were performed in deuteriochloroform, but one series at 30° was also made in *o*-dichlorobenzene.

*MO calculations.* We have calculated the energies, electron distributions, and orbital energies for the complete  $\pi$ -systems by the HMO method as well as by an  $\omega$ -method with  $\beta$ -variation,<sup>21</sup> and the same data for the partial structures X—C—Y and C(SR)<sub>2</sub> by the HMO method alone. The atom and bond integrals employed are shown in Table 4, and the results of the calculations in Table 5.

*Infrared spectra.* These were recorded in chloroform solution with a Perkin-Elmer Model 221 prism-grating instrument.

Table 2. Rate constants and thermodynamic parameters for 8 in *o*-dichlorobenzene (by the complete lineshape method).

<i>T</i> K	<i>k</i> sec <sup>-1</sup>	$\Delta G^\ddagger$ kcal/mole
375.9	11.2	20.36
377.8	13.9	20.31
385.7	18.3	20.53
391.5	24.3	20.63
395.4	30.6	20.67
399.4	36.8	20.74
403.6	45.8	20.79

$$E_a = 14.6 \pm 0.6 \text{ kcal/mole}$$

$$\log A = 9.6 \pm 0.3$$

$$\Delta H^\ddagger = 13.8 \pm 0.6 \text{ kcal/mole}$$

$$\Delta S^\ddagger = -17.3 \pm 1.4 \text{ eu}$$

$$\Delta G^\ddagger = 19.0 \pm 0.3 \text{ kcal/mole}$$

$\Delta H^\ddagger$  and  $\Delta S^\ddagger$  have been evaluated using the Eyring equation in the form

$$\log \frac{k}{T} = -\frac{\Delta H^\ddagger}{2.303RT} + \frac{\Delta S^\ddagger}{2.303R} + 10.3186$$

Table 3. Rate constants and thermodynamic parameters (in CDCl<sub>3</sub>) for the isomerisation of 3.

<i>T</i> K	<i>k</i> × 10 <sup>3</sup> sec <sup>-1</sup>	<i>k'</i> × 10 <sup>3</sup> sec <sup>-1</sup>	<i>K</i> <sub>e</sub>	$\Delta G^\ddagger$ kcal/mole	$\Delta G^{\ddagger'}$ kcal/mole
283	0.084 ± 0.003	0.137 ± 0.004	0.62	21.80 ± 0.02	21.52 ± 0.02
293	0.234 ± 0.003	0.378 ± 0.005	0.62	22.00 ± 0.01	21.71 ± 0.01
303	0.469 ± 0.011	0.745 ± 0.017	0.63	22.35 ± 0.01	22.07 ± 0.01
313	1.29 ± 0.03	1.98 ± 0.04	0.65	22.48 ± 0.01	22.17 ± 0.01
303 <sup>a</sup>	0.175 ± 0.005	0.268 ± 0.008	0.65	22.94 ± 0.02	22.68 ± 0.02

Forward reaction

Reverse reaction

<i>E</i> <sub>a</sub>	15.6 ± 0.9	15.3 ± 0.8 kcal/mole
log <i>A</i>	8.0 ± 0.6	7.9 ± 0.6
$\Delta H^\ddagger$	15.0 ± 0.9	14.7 ± 0.9 kcal/mole
$\Delta S^\ddagger$	-24.0 ± 2.9	-24.2 ± 2.8 eu

<sup>a</sup> In *o*-dichlorobenzene.

Table 4. Parameters for the LCAO-MO calculations ( $\omega=1.0$ ).

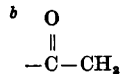
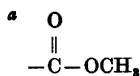
Atom (X)	$h_X^a$	Bond (C-X)	$k_{CX}^b$
C	0	C-C	1.0
$\dot{N}$	0.5	C $\equiv$ N	1.2
$\ddot{N}$	1.5	C-N	0.9
$\ddot{O}$	2.5	C-O	0.8
$\ddot{O}$	1.0	C=O	1.0
$\ddot{S}$	1.0	C-S	0.5

$$^a \alpha_X = \alpha_C + h_X \beta_{CC}$$

$$^b \beta_{CX} = k_{CX} \beta_{CC}$$

Table 5. Bond orders and  $\pi$ -electron energies (in units of  $\beta$ ).

Com- pound	$\Delta E_\pi$ (2) HMO	$\Delta E_\pi$ (3) HMO	$\Delta E_\pi$ (4) HMO	$p_{C=C}$		$p_{C=O}$		$r_{C_1-C_2}$ Å ( $\omega$ )
				HMO	$\omega$	HMO	$\omega$	
2	1.6193	0.8154	2.4232	0.6787	0.7889	0.6806	0.8361	1.374
5	1.6219	0.8450	2.3988	0.6932	0.7982	0.6374	0.7978	1.373
7	1.4794	0.9756	1.9832	0.7402	0.8166			1.369
8	1.5999	0.8014	2.3984	0.6744	0.7870	0.6455	0.8078	1.375
9	1.6963	0.7496	2.6430	0.6468	0.7636	0.6914 <sup>a</sup>	0.8402 <sup>a</sup>	1.379
						0.6574	0.8122	
10	1.6871	0.7264	2.6478	0.6331	0.7543	0.7316 <sup>b</sup>	0.8697 <sup>b</sup>	1.381
						0.6614	0.8135	
13	1.7182	0.9072	2.5292	0.7371	0.8356	0.6905	0.8535	1.366
14	1.5008	0.8230	2.1778	0.6814	0.7803	0.7068	0.8640	1.376
15	1.7374	0.9586	2.5162	0.7597	0.8475	0.8944 <sup>b</sup>	0.9801 <sup>b</sup>	1.364
						0.6587	0.8262	



## DISCUSSION

In the transition states of the rotations of these compounds the  $\pi$ -electrons of the double bond can be arranged in four different ways:

1. In a triplet state with one electron on X-C-Y and one on C(SR)<sub>2</sub>.
2. In a singlet state with the same electron distribution.
3. In a singlet state with two electrons in X-C-Y and a unit positive charge on C(SR)<sub>2</sub>.
4. In a singlet state with two electrons in C(SR)<sub>2</sub> and a unit positive charge on X-C-Y.

Model 1 requires a pre-exponential factor  $A$  in the Arrhenius rate law of the order of  $10^5$ - $10^6$  (Ref. 22), and it is therefore made less likely by our kinetic data for 3 and 8 (Tables 2 and 3). It is of interest in this connection

that Calvin and Alter<sup>3</sup> found an  $A$  value for the *cis* to *trans* isomerisation of *p*-amino-*p'*-nitrostilbene as low as  $10^5$ . The authors take this as an indication of a triplet mechanism, but in view of the similarities of their and our systems, one should expect the rotations to occur by the same mechanism.

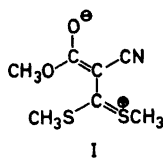
Table 6. IR bands ( $\text{cm}^{-1}$ ) measured in chloroform.

Compound	> C=O	-C≡N	> C=C <
1		2199	1520
2	1709	2204	1455
3	1708	2205	1450-1465
4	1709	2205	1450-1465
5	1670	2199	1460
6	—	2209	1425
7	—	2199	1505
8	1635	2199	1410-1445
9	1665, 1695		1520
10	1655		1478
11	1690, 1735		1445
12	1640		1480
13	1690		1410-1440
14	1655, 1690		1480
15	1710, 1660		1490
16	1705-1720		1530

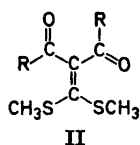
Models 2, 3, and 4 require normal pre-exponential factors, but it is not evident why a rotation that proceeds with a transition state of model 2 or 4, should be favoured by a combination of electron-donating substituents on  $C_1$  and electron-attracting substituents on  $C_2$ . The results of our HMO calculations favour model 3 over 2 and still more over 4 (Table 5), and so do considerations of substituent effects. We have therefore built our arguments on model 3. A fifth alternative, which ascribes the low barrier to quantum-mechanical tunnelling, can safely be excluded on the basis of the large masses involved.<sup>23</sup>

As is shown in Table 1, only five combinations of unequal X and Y give barriers that can be measured by the lineshape method. With the other combinations, except 15, the barriers are too high, *i.e.* sharp doublets are obtained for the methylthio groups up to 180-185°C, which means that coalescence must occur above 200°C. With 15, no shift difference was observed between the signals for the methylthio groups even at low temperatures, no matter which solvent was used.

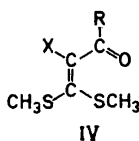
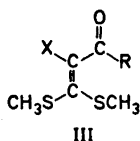
The five barriers, which fall between 17.5 and 24.5 kcal/mole, do not show a linear relation to the electron-attracting capacity of groups X and Y as given by their Hammett  $\sigma_p$ -values. A comparison of 8, 9, and 10 (X=PhCO) shows that the barrier-lowering effect increases in the order Y = CN < CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub> < COCH<sub>3</sub>, whereas the order of their  $\sigma_p$ -values is CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub> (0.45) < CH<sub>3</sub>CO (0.50) < CN (0.66).<sup>24</sup>



One could envisage the low barriers as being connected with a low double bond character, caused by great weight of such limiting structures as (I). It is evident from the infrared spectra that these compounds are polarised in the direction indicated by (I). The stretching frequencies of carbonyl groups in ester, acetyl, and benzoyl derivatives are 40–60  $\text{cm}^{-1}$  lower than normal (Table 6). In the symmetrical compounds *14* and *16* two carbonyl bands are observed. This can be caused by mechanical coupling, but a contributing factor may also be an *S-cis-S-trans* arrangement of the carbonyl groups with respect to the  $\text{C}_1-\text{C}_2$  bond (II). This arrangement has been demonstrated for 1,1-bis-acetyl-2,2-bis-dimethylaminoethylene.<sup>7</sup> In the dicyano compound *6* a doubling of the stretching frequency of the cyano groups is observed in the solid phase,<sup>13</sup> but not in solution. The cyano group stretching frequencies are lower than in saturated ( $\nu_{\text{CN}}$  ca. 2250  $\text{cm}^{-1}$ ) and simple conjugated nitriles ( $\nu_{\text{CN}}$  ca. 2220  $\text{cm}^{-1}$ ).



The double bond stretching vibration can in general be assigned to a strong and rather broad band in the region 1430–1530  $\text{cm}^{-1}$ . The variable position of this band and the lack of correlation with barrier heights indicate that it is modified by coupling with neighbouring vibrations. Gompper *et al.*<sup>8,25,26</sup> and Jensen and Henriksen<sup>13</sup> have previously observed similar low frequencies in analogous compounds. Since coupling is strongest between collinear neighbouring vibrators with not too unlike frequencies, carbonyl groups in structures like (III) will give rise to strong coupling and in (IV) to somewhat weaker. That means that in such structures the carbonyl frequencies are raised and the double bond frequencies lowered with respect to what should be expected on ground of force constants and consequently  $\pi$ -electron delocalisation, alone. Coupling with the  $\text{C}_1-\text{S}$ -bond vibrations will work in the opposite direction, but their frequencies are so much lower than the double bond frequency that





this effect can be expected to be smaller. The sulphone *11* shows normal unconjugated ester and benzoyl carbonyl frequencies and also the expected sulphonyl frequencies (triplet at 1130–1180, singlet in the region 1310–1340  $\text{cm}^{-1}$ ). In the double bond region only weak, sharp absorption bands are visible, most of them probably aromatic ring-stretching bands. It is possible that the polarity of the  $\text{C}_1\text{--C}_2$  bond is nearly eliminated by the opposing polarities of the substituents.

However, it seems unlikely that the polarisation of the  $\text{C}_1\text{--C}_2$  bond in the bis-alkythio ethylenes is in any way linearly related to the lowering of the barrier from that of ethylene (65 kcal/mole) to that of a normal single bond. Our MO calculations by the HMO method give  $\pi$ -bond orders between 0.63 and 0.76 ( $p_\pi$  HMO) and by the  $\omega$ -method between 0.75 and 0.85 ( $p_\pi \omega$ ). Since the HMO method tends to exaggerate conjugation effects, the  $p_\pi \omega$ -values should be the more reliable ones, and the conclusion is that the double bond character is essentially preserved in these compounds. By use of the  $p_\pi \omega$ -values and the bond order-bond length relation proposed by Coulson,<sup>27</sup> bond lengths between 1.36 Å and 1.38 Å are obtained (Table 5). It is interesting to compare these results with the length of 1.36–1.37 Å observed for the double bond joining the cyclopropene and cyclopentadiene rings in two calicene derivatives,<sup>28,29</sup> since low barriers to rotation around this bond have been observed in similar compounds.<sup>30</sup>

With model 3 for the transition state, the low double bond barriers are related to the capacity of  $\text{X--C--Y}$  to stabilise an extra electron pair and of  $\text{C}(\text{SR})_2$  to stabilise a positive charge. The  $\pi$ -electron energy contribution to the barrier,  $\Delta E_\pi$ , is given by the expression:

$$\Delta E_\pi = E_{\pi, \text{XYC}=\text{C}(\text{SR})_2} - (E_{\pi, \text{XYC}\ominus} + E_{\pi, (\text{RS})_2\text{C}\oplus})$$

With model 3, all bonding and no antibonding orbitals are occupied, whereas with model 2 one and with model 4 two electrons are transferred from the highest bonding orbital of  $\text{X--C--Y}$  to the lowest antibonding orbital of  $\text{C}(\text{SR})_2$ , with accompanying increase in  $\Delta E_\pi$  (Table 5).

The  $\Delta E_\pi$  values for model 3 obtained by the HMO method give a reasonable linear correlation with  $\Delta G^\ddagger$  (Fig. 1). It seems as if  $\Delta E_\pi$  could have a

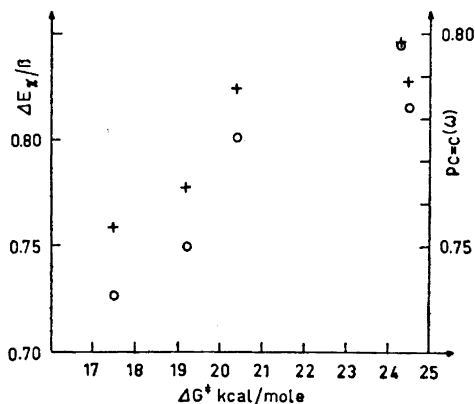


Fig. 1. Correlation between experimental barriers ( $\Delta G^\ddagger$ ), bond orders ( $p_{\text{C}=\text{C}} \omega$ , +), and calculated  $\pi$ -energy contributions to the barriers ( $\Delta E_\pi$ , ○).

certain predictive value, so that, with the same parameters,  $\Delta E\pi > 0.87 \beta$  should indicate  $\Delta G^\ddagger > 25$  kcal/mole. Unlike *N,N*-dimethylthioamides,<sup>31</sup> the bis-methylthioethylenes give a reasonable correlation between  $\Delta G^\ddagger$  and the  $\pi$ -bond order of the pivot bond (Fig. 1). Finally, the importance of electron-donating substituents for a low barrier is indicated by the high barrier in the disulphone 11.

Both the complete lineshape investigation of  $\delta$  in *o*-dichlorobenzene (Table 2) and the isomerisation of 3 in deuteriochloroform (Table 3) give large negative entropies of activation, in striking contrast to the values close to zero recently observed for the internal rotation in *N,N*-dimethylamides and -thioamides.<sup>32-34</sup> This difference is in good agreement with the assumed changes in polarity on rotation. In the ethylenes, the increased polarity should lead to a more strongly solvated transition state, whereas in amides the rotation of the dimethylamino group 90° out of the plane should rather decrease the polarity and thus lead to a less organised transition state. In later work we will report on the effect of solvent polarity on rates of rotation in similar systems.

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