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The Barriers to Internal Rotation in N,N-Dimethylcyclopropanecarboxamide and -carbothioamide, and the Ultraviolet Spectrum of the Carbothioamide

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The thermodynamic parameters for the hindered rotation of the dimethylamino group in N,N-dimethyl-cyclopropanecarboxamide and -carbothioamide have been determined by NMR technique. The results indicate a conjugation between the cyclopropane ring and the carbothioamide thiocarbonyl group. The ultraviolet spectrum of the carbothioamide shows a bathochromic shift of the $\pi \rightarrow \pi^*$ band but a hypsochromic shift of the $n \rightarrow \pi^*$ band. This is discussed in relation to the charge distribution in the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ excited states.

The ability of the cyclopropyl group to conjugate with double bonds is manifested in infrared [1] and ultraviolet [2] spectra, in dipole moments,[3] and also in chemical properties.[4] In particular, the conjugation has been found to be effective with positive centra as in cyclopropylmethylcarbonium ions.[5] It has also been observed [6,7] that the conjugating capacity of the group R in $R{\cdot}CX{\cdot}N(CH_3)_2$ (X = O or S) has a considerable influence on the barrier hindering the rotation of the dimethylamino group. Thus, for N,N-dimethylcarbothioamides, $\Delta G^{\ddagger}$ values between 11.5 and 24.0 kcal/mole were observed, depending only on the nature of R. For this reason it was considered of interest to measure the barriers in N,N-dimethylcyclopropanecarboxamide and its thio analogue. Since the ultraviolet spectra of thioamides are also greatly influenced by R,[8] it was considered worthwhile to record and discuss the spectra of these compounds.

EXPERIMENTAL METHODS

Materials. N,N-Dimethylcyclopropanecarboxamide was prepared according to Roberts *et al.*[9] The NMR spectrum of this compound was in agreement with the expected structure. The cyclopropyl protons gave three groups of complex signals around $\tau = 8.3$ (1H), $\tau = 9.1$ (2H), and $\tau = 9.3$ (2H) in *o*-dichlorobenzene.

N,N-Dimethylcyclopropanecarbothioamide. The carboxamide (12.4 g) and phosphorus pentasulphide (12.4 g) were refluxed in toluene (100 ml) for 3 h. The solution was filtered,

and the solid residue extracted with boiling toluene. The combined toluene solutions were distilled in vacuum, and at 136–138° (22 Torr) a yellow oil was obtained, which crystallized in the condenser. The product (1.4 g, 10 % yield) crystallized from toluene-heptane at −30° as colourless prisms, m.p. 53.5–54°. (Found: C 54.6; H 8.48; N 10.5; S 24.2. $C_6H_{11}NS$ (129.23) requires C 55.8; H 8.58; N 10.8; S 24.8). Before the measurements the product was further purified by vacuum sublimation. The cyclopropyl protons gave three groups of complex signals around $\tau = 8.2$ (1H), $\tau = 8.8$ (2H), and $\tau = 9.2$ (2H) in *o*-dichlorobenzene.

N,N-Dimethylisobutyramide and its thio analogue were prepared in the same way. The thioamide, which has not been described earlier, was obtained as a pale yellow liquid, b.p. 114–119° (14 Torr.).

Solvents. *o*-Dichlorobenzene for NMR spectra was purified by vacuum distillation. Heptane for ultraviolet spectra was shaken with conc. sulphuric acid followed by water, dried, and distilled through a 50 cm Vigreux column.

Recording of the NMR spectra. The spectra were obtained with a Varian A-60 spectrometer equipped with a Varian V-6031 variable temperature probe and temperature controller. The spectra were recorded with a sweep width of 2 cps/cm and at a rate of 0.2 cps/sec. The amplitude of the radiofrequency field was kept well below the level where saturation effects could be observed. In each experiment, the lineshapes were recorded at 10–12 different temperatures. At each temperature 7–10 different spectra were recorded with both upfield and downfield direction of the recorder. The spectra were recorded against tetramethylsilane as an internal standard.

Temperature measurements. With *o*-dichlorobenzene as solvent, the temperature could be obtained from the chemical shift between the CH and OH signals from ethylene glycol (above room temperature) or acidified methanol (below room temperature), contained in narrow concentric capillaries in the sample tubes. For the carboxamide without solvent, the amide and methanol CH_3 signals overlapped. Instead, a capillary containing methylene chloride, tetradeuteromethanol, and hydrochloric acid was used, and the temperature was obtained from the shift between the CH_2Cl_2 and OH proton signals. In all cases, the shifts were calibrated, using the ordinary Varian ethylene glycol and methanol samples. In this way an accuracy of about ± 0.3°C could be obtained.

Ultraviolet spectra were recorded with a Cary Model 15 recording spectrophotometer.

CALCULATION OF THE THERMODYNAMIC PARAMETERS

For evaluation of the rate constants from the NMR lineshapes, the ratio method of Rogers and Woodbrey [6] was used. In all cases the overlap of the two N-methyl signals was negligible when the rate of exchange was low, and therefore the approximations involved in the ratio method should not seriously affect the thermodynamic parameters.

The logarithms of the rate constants were fitted against the inverse temperatures in a least squares plot to give the Arrhenius parameters E_a and $^{10}\log A$ (1). The free energy of activation, $\Delta G^{\ddagger}$, was obtained from the Eyring equation (2), and it was evaluated at the collapse temperature T_c. The same applies for the enthalpies (3) and entropies (4) of activation.

$$^{10}\log k = -\frac{E_a}{2.303\ RT} + {}^{10}\log A \tag{1}$$

$$\Delta G^{\ddagger} = -2.303\ RT_c \cdot {}^{10}\log \frac{hk}{kT_c} \tag{2}$$

$$\Delta H^{\ddagger} = E_a - RT_c \tag{3}$$

$$\Delta S^{\ddagger} = \frac{\Delta H^{\ddagger} - \Delta G^{\ddagger}}{T_c} \tag{4}$$

Table 1. Thermodynamic parameters for $C_3H_5 \cdot CX \cdot N(CH_3)_2$.

X	Solvent	ν_A cps	ν_B cps	E_a kcal/mole	log A	$\Delta G^{\ddagger}$ kcal/mole	$\Delta H^{\ddagger}$ kcal/mole	$\Delta S^{\ddagger}$ e.u.	T_c °K
O	ODC [a]	178.4	171.6	12.7 ± 0.4	10.1 ± 0.3	16.4 ± 0.4	12.1 ± 0.4	−13.8 ± 2.6	311.4
O	—	188.6	171.3	12.3 ± 0.1	10.0 ± 0.1	16.1 ± 0.1	11.7 ± 0.1	−13.7 ± 0.6	319.7
S	ODC	201.8	192.4	17.1 ± 0.3	11.8 ± 0.2	18.4 ± 0.3	16.4 ± 0.3	− 5.3 ± 1.7	356.8

[a] ODC = *o*-dichlorobenzene (molar fraction of solute = 0.333).

The results are shown in Table 1. The errors in E_a and log A are standard deviations from the least squares plot, and the errors in $\Delta H^{\ddagger}$ and $\Delta G^{\ddagger}$ are assumed to be the same as in E_a. The error in $\Delta S^{\ddagger}$ is twice the deviation in E_a divided by T_c.

DISCUSSION

Steric effects. It is obvious that steric effects can play an important role in determining the barriers to internal rotation in amides and thioamides. In the planar state, crowding will lower the barrier, and in the transition state the effect is the opposite, as has been shown by Mannschreck [11] and Staab.[12] In the molecules investigated here, the geometry can be expected to be similar to that of cyclopropanecarbaldehyde. Bartell and Guillory [13] have shown by electron diffraction that this compound consists of nearly equal amounts of *cis* and *trans* forms, in both of which the plane of the formyl group bisects the cyclopropyl group along the symmetry plane. In this way the maximum overlap is obtained between the π orbital of the carbonyl group and the carbon-carbon "banana" bonds [14] in the cyclopropane ring. In the dimethylamide and -thioamide the *cis* and *trans* forms are not equally probable. In the conformation in which the carbonyl (thiocarbonyl) group is *cis* with respect to the ring, molecular models show that no steric interference exists, whereas in the *trans* conformation one of the N-methyl groups comes very close to two ring hydrogen atoms. Thus the molecules have one state, which is not crowded, and the measured barriers should be free from steric effects (Fig. 1).

The effect of conjugation on the barriers can conveniently be defined as the difference between the energies of interaction of the substituent R with the (thio)-amide group on the one hand and the (thio)-carbonyl group on the other. Generally, increasing conjugation capacity of the group R will lower the barrier, since the energy of interaction with the (thio)-carbonyl group will be larger than crossconjugation with the (thio)-amide group. In order to detect the effect of conjugation in the present case, one should compare the measured barriers, and in particular the $\Delta G^{\ddagger}$ values, with barriers from simple and conjugated N,N-dimethylamides and -thioamides. For dimethyl-

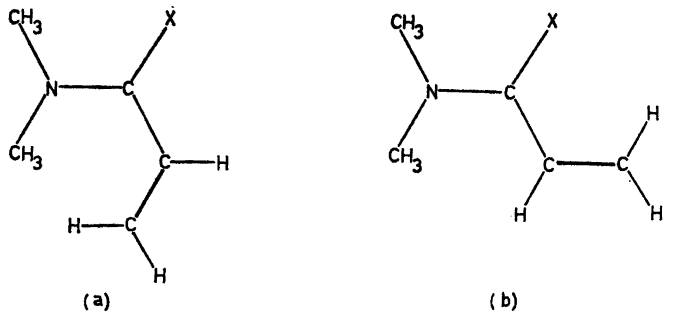

Fig. 1. Trans (a) and *cis* (b) form of dimethyl(thio)amide, seen from above the plane bisecting the cyclopropane ring. The ring is marked out with a heavier line.

formamide $\Delta G^{\ddagger}$ is 21.0 kcal/mole, for dimethylacrylamide 16.1 kcal/mole and for dimethylbenzamide 15.3 kcal/mole. Thus, the cyclopropyl group should be as efficient as a double bond in lowering the barrier. However, alkyl groups also have a rather strong influence on the barrier. Thus, dimethylacetamide has $\Delta G^{\ddagger}$ 17.4 kcal/mole and dimethylpropionamide 16.7 kcal/mole. In the latter case a small steric effect may contribute to the lowering of the barrier, but the results do not unequivocally support a π type of conjugation between the cyclopropyl and amide groups.

For dimethylthioformamide $\Delta G^{\ddagger}$ is 24 kcal/mole, and for dimethylthioacetamide 21.6 kcal/mole. Unfortunately, the barriers for the thioacrylamide and thiopropionamide are not known, but it may be meaningful to compare with dimethylthiobenzamide ($\Delta G^{\ddagger} = 18.4$ kcal/mole). Thus, the cyclopropane ring in this case is as efficient as a benzene ring. The $\Delta G^{\ddagger}$ values for the carboxamides are taken from Ref. 6 and those for the carbothioamides from Ref. 7. The barriers of the carboxamides have been measured without solvent, or, in the case of dimethylbenzamide, in methylene chloride solution. Because of its importance to the present discussion, dimethylbenzamide was investigated in *o*-dichlorobenzene solution and gave $\Delta G^{\ddagger} =$ 14.9 kcal/mole.

The uncertainty in the effect of the alkyl groups made an extension of the available material desirable. Since the isopropyl group has some similarity to the cyclopropyl group, N,N-dimethylisobutyramide and its thio analogue were subjected to NMR investigation. Unfortunately, overlap of the N-methyl proton signals and the methine proton septet in both cases prevented a detailed study of the lineshapes, but ν_A, ν_B and T_c could readily be measured. The $\Delta G^{\ddagger}$ values obtained from these results are shown in Table 2.

These results show that in the amide the cyclopropyl and the isopropyl groups are about equally barrier-lowering. Even if the steric effect of the isopropyl group is larger, the results do not leave much conjugation effect to the cyclopropyl group. On the other hand, in the thioamide, the conjugation with the cyclopropyl group seems to lower the barrier with at least 1 kcal/mole.

The specific capacity of the cyclopropyl group to stabilize an adjacent positive center does not seem to be of importance here, since molecular orbital calculations by a modified ω-method [15] give the result that the π electron density on the (thio)-carbonyl carbon atom is nearly unchanged when the dimethylamino group is turned out of conjugation.

Table 2. NMR parameters and $\Delta G^{\ddagger}$ values for $(CH_3)_2CH{\cdot}CX{\cdot}N(CH_3)_2$.

X	Solvent	$\nu_A - \nu_B$* cps	T_c°K	$G^{\ddagger}$ kcal/mole
O	ODC	3.9	299	16.2
S	ODC	12.4	370	19.3

* Measured at T_c as linewidth at half maximum amplitude.

Table 3. Calculated π electron distribution in different states of the thioamide group.

State	q_S	q_C	q_N
Ground	1.311	0.874	1.816
$\pi \rightarrow \pi^*$	1.014	1.203	1.783
$n \rightarrow \pi^*$	1.655	1.437	1.908

Entropy effects. N,N-Dimethylcyclopropanecarboxamide has been investigated both in *o*-dichlorobenzene and without solvent, the solid carbothioamide only in *o*-dichlorobenzene. The carboxamide in both cases has a lower entropy of activation than the carbothioamide, *i.e.* the latter shows a greater loss of order on rotation, which may be due to a stronger solvation in the planar state. This is in agreement with the generally stronger polarization of carbothioamides.[16]

Ultraviolet spectra. The carboxamide showed no selective absorption at wavelengths above 205 nm, which is not surprising since no absorption bands in the near ultraviolet have been reported for acrylamide [17] or crotonamide.[18] The carbothioamide, on the other hand, showed a $n \rightarrow \pi^*$ band at 358 nm ($\varepsilon = 48$) and a $\pi \rightarrow \pi^*$ band at 277 nm ($\varepsilon = 12\,300$) in heptane. A comparison with N,N-dimethylthioacetamide,[8] with the $n \rightarrow \pi^*$ band at 365 nm and the $\pi \rightarrow \pi^*$ band at 272 nm is somewhat confusing, since in general both bands undergo red shift on conjugation.[19] It is of interest, however, that Rogers [2] has noted a similar behaviour of the corresponding bands in the ultraviolet spectrum of cyclopropyl methyl ketone. The charge distribution in the ground state and the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ excited states (Table 3, calculated with parameter set 4 of Ref. 15) may be of some importance in this connection. The results should then indicate that the stabilization of the excited states by conjugation with the cyclopropane ring is lower, the higher the negative charge on the carbon atom.

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