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*Fig.1.*The complex ion[Co((OH)$_2$(NH$_3$)$_4$Co)$_3$]$^{6+}$.

chlorine atom is on the three-fold axis and 2 water and 2 chlorine (N – Cl 3.41 – 3.45 Å) are statistically arranged. There are contacts from this layer to a statistical Cl – H$_2$O layer around the zero plane (3.26 – 3.43 Å). The nitrogens from both sides of the complex contact the same chlorine (3.11 – 3.48 Å). The chlorine in close packing contacts a water molecule on the three-fold axis (3.21 Å).

In the direction of the three-fold axis the oxygen atoms on one side of the complex have contact to this water molecule (3.04 Å) and on the opposite side to a chlorine water layer (2.99 Å).

In the chlorine-water layer perpendicular to the three-fold axis the shortest distances of contact are Cl – H$_2$O 3.06 Å and H$_2$O – H$_2$O 2.94 Å.

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The Temperature Dependence of the ^{1}H NMR Spectra of 1,1-Substituted Thiosemicarbazides. Calculation of Energy Barriers

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NMR studies of the conformation, the barriers to rotation about the N – N bonds, and the barriers to inversion at the nitrogen atoms of hydrazine derivatives have been of current interest in recent years (*cf.* Refs. 1 – 6 and references cited therein). The benzyl derivatives have been most studied owing to the simplicity of the spin system of the exchanging protons. This communication reports the energy barriers for the intramolecular exchange processes of a series of 1,1-dibenzylthiosemicarbazides (IIa-e). For comparison, the ^{1}H NMR spectra of 1,1-dibenzyl-4-*tert*-butylsemicarbazide (Ie), 1,1-dibenzyl-4-*tert*-butylselenosemicarbazide (IIIe), 1,1-diisopropyl-4-*tert*-butylthiosemicarbazide
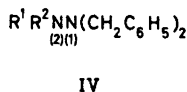
(IIf), and 1,1-diisobutyl-4-*tert*-butylthio-semicarbazide (IIg) were also investigated.

$$\overset{\overset{\text{X}}{\|}}{\text{RHNCNHN}}(\text{CH}_2\text{C}_6\text{H}_5)_2$$
$$\text{(2) (1)}$$

I : X = O

II : X = S

III : X = Se
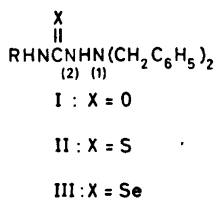
R	Me	Et	Bz	*i*Pr	*t*Bu
I—III	a	b	c	d	e

Hydrazine and its derivatives probably have a dihedral angle close to 90° (*cf.* Refs. 4 and 7 and references cited therein), and the following discussion is based on this assumption.

$$\text{R}^1\text{R}^2\text{NN}(\text{CH}_2\text{C}_6\text{H}_5)_2$$
$$\text{(2)(1)}$$

IV

The slow exchange process may be a rotation about the N — N bond or an inversion at a nitrogen atom. In order to compare the magnitudes of the energy barriers for these two processes, Dewar and Jennings [1,2] have examined the temperature dependence of the ¹H NMR signals from the methylene protons of compounds of type IV with $R^1 = R^2$. In this type of compound, the methylene protons of a benzyl group can be non-equivalent only if inversion is slow at N(1), and the benzyl groups can be non-equivalent only if both rotation about the N — N bond and inversion at N(2) are slow. The spectrum of IV $(R^1 = R^2 = C_6H_5CH_2)$ exhibited [1] two AB systems at low temperature, *i.e.* both inversion and rotation were slow. The temperature dependence of the spectrum revealed that the barrier to inversion (which was of the same magnitude, 8 kcal/mol, as that found [2] for N(1) in IV with $R^1 = R^2 = H$) was smaller than the barrier to rotation, which consequently could not be measured. When $R^1 \neq R^2$ only a single AB pattern has been observed,[2,3]

which may be due to (*1*) slow inversion at N(1) with fast rotation about the N — N bond and planar configuration or fast inversion at N(2), or (*2*) slow rotation about the N — N bond with fast inversion (or planar configurations) at the nitrogen atoms. The energy barriers increase with increasing size of the substituents [2-4] and are in all cases greater than the inversion barriers of N(1) in IV with $R^1 = R^2$. This behaviour strongly indicates that the observed non-equivalence of the methylene protons of IV $(R^1 \neq R^2)$ is due to hindered rotation about the N — N bond (case (*2*)).

The signals from the methylene protons next to N(1) of the compounds I — III (a — e) form *one* AB system at low temperature (*cf.* Fig. 1); *i.e.*, the benzyl groups are
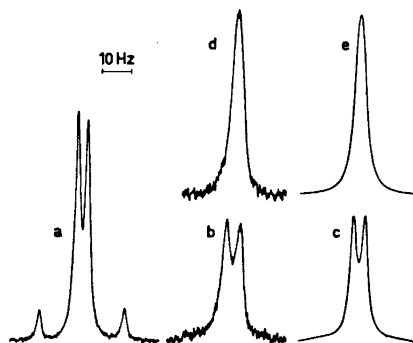

Fig. 1. Calculated and experimental spectra of the *N*-CH₂ protons of 1,1-dibenzyl-4-*tert*-butylthiosemicarbazide (IIe) in nitrobenzene-d_5. a, b, and d: Experimental spectra at 30°, 70° and 85°C, respectively. c and e: Calculated for $\tau = 0.046$ and 0.0152 sec, respectively.

equivalent, but the methylene protons of each group are magnetically non-equivalent. This property indicates an exchange process of type (*1*) or (*2*), as defined above for IV with $R^1 \neq R^2$. Hindered rotation about the C — N(2) bond cannot be responsible for the observation of an AB pattern. Hindered rotation about the N(1) — C bonds could lead to non-equivalence of the N(1) — CH₂ protons but seems unlikely.

The energy barriers for the compounds I — III (a — e), listed in Table 1, have been derived from the temperature dependence of the signals from the N(1) — CH₂ protons by a line shape analysis using density

Table 1. Energy barriers [a] for the compounds I–III and spectral parameters [b] without exchange of the non-equivalent protons.

Compound	Solvent	Δ_{AB}	J_{AB}	$\Delta G^{\ddagger}{}_{25°C}$ (kcal/mol)	E_a (kcal/mol)	$\log A$	$\Delta H^{\ddagger}{}_{25°C}$ (kcal/mol)	$\Delta S^{\ddagger}{}_{25°C}$ (e.u.)
IIa	NB	7.7	12.9	17.3 ± 0.1	16.5 ± 1.0	12.2 ± 0.7	15.9 ± 1.0	− 4.7 ± 3.4
IIb	NB	9.6	12.6	17.2 ± 0.1	15.7 ± 1.1	11.7 ± 0.7	15.1 ± 1.1	− 7.2 ± 3.6
IIc	NB	9.3	12.8	17.3 ± 0.1	15.2 ± 0.8	11.2 ± 0.5	14.6 ± 0.8	− 9.3 ± 2.5
IId	NB	10.1	12.5	17.6 ± 0.1	17.6 ± 0.4	12.8 ± 0.2	17.0 ± 0.4	− 2.2 ± 1.2
IIe	NB	11.9	12.4	18.3 ± 0.1	19.1 ± 1.4	13.4 ± 0.8	18.5 ± 1.4	0.9 ± 4.2
IIe	DMSO-d_6	10.3	12.3	18.4 ± 0.1	19.4 ± 0.5	13.6 ± 0.3	18.9 ± 0.5	1.6 ± 1.7
Ie	CDCl$_3$	13.1	12.8	14.8 ± 0.1	12.9 ± 0.6	11.4 ± 0.4	12.3 ± 0.6	− 8.3 ± 2.2
IIIe	NB	10.0	12.6	18.6 ± 0.1	18.9 ± 1.1	13.1 ± 0.7	18.3 ± 1.1	− 0.9 ± 3.4
IIf	NB	3.3		22.0^c				
IIg	NB	5.4		19.6^c				

[a] The limits include only standard deviations from the least squares treatment (90 % confidence limits were used).[12] [b] In Hz at 60 MHz. NB = nitrobenzene-d_5. [c] Estimated values of $\Delta G^{\ddagger}$ at coalescence. $T_c = 399°$K for IIf and 363°K for IIg.

matrix theory in the form of eqn. (4) of Heidberg *et al.*[8] The values of $\Delta G_c{}^{\ddagger}$ (at coalescence) for the compounds IIf and IIg were estimated from eqn. (6) of Gutowsky and Holm.[9,10] The energy barriers increase with increasing size of the substituents and are of the same order of magnitude as found for N,N'-dibenzyl-N,N'-dibenzoylhydrazine.[3] On this basis, the exchange process is, as for IV with $R^1 \neq R^2$, tentatively assigned to type (2), *i.e.* slow rotation about the N−N bond. Further investigation of the ¹H NMR spectra of thiosemicarbazides is in progress.

Experimental. The compounds were prepared according to previously described methods[11] and have been fully characterized by analysis and IR and NMR spectra.

The ¹H NMR spectra were recorded at 60 MHz on a Varian A60A spectrometer equipped with a variable temperature controller. The temperature was determined by measuring the chemical shift difference between the signals from the CH$_2$ and OH protons of an ethylene glycol sample. The mean lifetime τ was found, as previously described,[12] by comparison of experimental and calculated spectra. The activation energy for the intramolecular exchange was obtained from the Arrhenius equation by the method of least squares, and $\Delta G^{\ddagger}$ was found from the Eyring equation (assuming unity for the transmission coefficient). The calculations of the line shapes and energy barriers were performed on an IBM 7094 computer.

The coupling constants J_{AB} without exchange were temperature independent, whereas the chemical shift differences $\Delta_{AB} = \nu_A - \nu_B$ without exchange depended on the temperature (*cf.* Fig. 2), and the values used in the
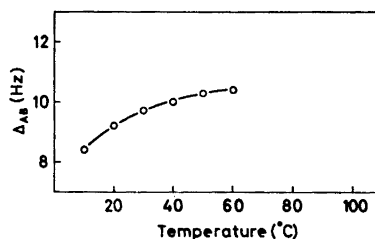

Fig. 2. The chemical shift difference (at 60 MHz) without exchange of the non-equivalent methylene protons of 1,1-dibenzyl-4-*tert*-butyl-thiosemicarbazide (IIe) in nitrobenzene-d_5 as a function of the temperature.

calculation of the line shapes were corrected accordingly (by extrapolation from graphs of the type shown in Fig. 2). As was also observed by, *e.g.*, Dewar and Jennings,[1] the signals from the N-CH$_2$ protons were more broadened than the TMS signal at low temperatures.

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