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Derivatives of Hydrazine

V. *cis-trans* Isomerism, Dipolar Structure, and Magnetic Nonequivalence of the Isopropyl Methyl ^{1}H NMR Signals of Acyl and Thioacyl *N,N*-Diisopropylhydrazines

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The ^{1}H NMR spectra of acyl *N,N*-diisopropylhydrazines in different solvents indicate that these substances exist as mixtures of *cis*- and *trans*-forms. The equilibrium appears to be determined by the steric influence of the acyl group. Formyl *N,N*-diisopropylhydrazine exemplifies a case (A) in which the diisopropylamino group is mainly in the *trans*-position to the carbonyl group. Pivaloyl *N,N*-diisopropylhydrazine has another type of non-polar structure (B) in which the same groups are in the *cis*-positions. This may be explained by the presence of the bulky *tert*-butyl group, which must occupy the *trans*-position to the diisopropylamino group. In the case of thioacyl *N,N*-diisopropylhydrazines a different equilibrium occurs. One of the isomers has the diisopropylamino group *trans* to the thiocarbonyl group and parallels case A above. The other isomer is a tautomeric dipolar structure (C) and has no counterpart within the oxygen analogues. Even in this case a steric influence operates as thioformyl *N,N*-diisopropylhydrazine is mainly nonpolar, but thiopivaloyl *N,N*-diisopropylhydrazine is exclusively dipolar. Parallel cases and several examples of magnetic nonequivalence of the isopropyl methyl protons of the forms A and C are discussed.

From studies of the reactivity of *N*-isothiocyanatodiisopropylamine [1–3] a great variety of derivatives of *N,N*-diisopropylthiocarbazic acid with the general structure $Pr^i_2N-NH-CS-R$ were obtained. Proton magnetic resonance investigations of $CDCl_3$ solutions of these compounds revealed that an equilibrium had sometimes occurred between species corresponding to the nonpolar form shown above and isomers to which a dipolar from $Pr^i_2NH-\overset{+}{N}=C\begin{matrix}\diagup S^- \\ \diagdown R\end{matrix}$ could be assigned. This result was not entirely unexpected in view of the recent result [4] that complete conversion to the dipolar form is

the rule both in the solid state and in solution when R = imidazole. Furthermore, the ^{1}H NMR spectra revealed that the methyl groups of both the diisopropylamino group of the nonpolar form, and of the diisopropylammonium group of the dipolar form, were in some instances nonequivalent. The methyl signals were then observed as two superimposed doublets instead of the usual single doublet expected from the coupling with the methine proton of the isopropyl group. In order to determine which conditions are necessary for these phenomena to occur some simple thioacyl *N,N*-diisopropylhydrazines were prepared and the ^{1}H NMR spectra compared to those of the oxygen analogues with the general structure $Pr^i_2N-NH-CO-R$. Since the latter compounds give ^{1}H NMR spectra which are easily interpreted as due to a mixture of *cis*- and *trans*-isomers, they will be considered first.

The chemical shifts and coupling constants obtained from the ^{1}H NMR spectra of formyl *N,N*-diisopropylhydrazine (I) in different solvents are summarized in Table 1. It should be realized that the figures given in the

Table 1. Chemical shifts[a] (τ, ppm) and coupling constants (*J*, Hz) of formyl *N,N*-diisopropylhydrazine (I).

IA IB

Solvent	Conc. %	Temp. °C	Form (%)	NPr^i_2			HCONH		
				CH_3(2)	CH(7)	*J*	CH	NH	*J*
CCl_4	10	40	A (100)	8.95	6.83	6.4	1.94(2)	1.14(2)	10.7
$CDCl_3$	7	40	A (85)	8.96	6.87	6.4	1.84(2)	2.85(2)	10.6
			B (15)	8.91	6.85	6.2	1.81(1)	−obs	0
«	«	−40	A (96)	8.92	6.80	6.4	1.80(2)	1.64(2)	10.6
			B (4)	−obs	−obs	−obs	1.80(1)	−obs	0
CH_3OH/ CD_3OD	6	40	A (57)	8.98	6.79	6.5	1.83(2)	1.62(2)	10.7
			B (43)	8.96	6.82	6.4	1.86(1)	1.45(1)	0

[a] The values given in the table are the centers of the multiplets. The multiplicities are given in parentheses. The standard errors are ±0.1 Hz on the coupling constants, and 0.01 ppm on the chemical shifts.

table are very probably weighted averages of the values of differently associated species existing in rapid equilibrium. The presence of associated species is strongly indicated by the observation that the infrared spectrum of a saturated solution of (I) in $CHCl_3$ exhibits two NH stretching absorptions at *ca.* 3100

and 3200 cm^{-1}, but solutions below 5 % concentration show only one such absorption at 3320 cm^{-1}. However, apart from a shift of the signal from the NH proton towards higher field only very small changes were observed in the ^1H NMR spectrum if a saturated (70 %) solution of (I) in $CDCl_3$ was diluted to *ca.* 5 %. The degree of association, therefore, cannot be a decisive factor in determining the nature of the ^1H NMR spectrum obtained.

By analogy of formamides [5-8] it was expected that both a *cis*- and a *trans*-form should occur. This isomerism arises because of resonance interaction, which causes the frequency of rotation about the central nitrogen-carbonyl bond to decrease. In this way separate signals are expected from form A (with the NH proton *trans* to the formyl proton) and from form B (with the corresponding groups in the *cis* position). These two forms are shown at the top of Table 1. The presence of any appreciable amount of an iminol form [9] is excluded by the infrared spectrum which, in the range between 1500 and 2000 cm^{-1}, displays only a strong CO stretching absorption at 1700 cm^{-1} and no C=N stretching absorption.

The simplest ^1H NMR spectrum of (I) was obtained when CCl_4 was used as solvent. By shaking with deuterium oxide it was confirmed that the AB-pattern in the low-field region arises from the coupling of the formyl proton with the NH proton. The coupling constant, $J = 10.7$ Hz, being quite close in value to the *trans* coupling constants of the *H*CON*H* system of the structurally related formamides (formamide [10] 12.9 Hz, *N*-alkylformamides [8] 13.8—14.4 Hz, formanilide [6] 11.0 Hz, and substituted formanilides [11] 11.0—11.8 Hz), allows the isomer present in tetrachloromethane to be assigned to the A form (Table 1). The identification of the signals arising from the protons of the diisopropylamino group is then straightforward.

When the dielectric constant of the solvent was raised (ε-values for CCl_4, $CDCl_3$, and CH_3OH are 2.24, 4.81, and 32.6, respectively) the spectrum was transformed from that of the pure A form into that of a mixture containing approximately equal amounts of the A and the B forms. That the formyl proton and the NH proton are not coupled to each other to a measurable extent in the B form is unexpected since the corresponding *cis*-coupling constants of the *H*CON*H* system in formamides are small, but observable (formamide [6] 2.0 Hz, *N*-alkylformamides [8] 1.8—2.3 Hz, formanilide [6] 2.0 Hz, and substituted formanilides [11] 1—2.2 Hz). To verify that these protons were not coupled it was necessary to displace the doublet originating from the formyl proton of the A form relative to the partly overlapping unsplit signal due to the formyl proton of the B form. Only in this way could it be ascertained that the latter signal was not, alternatively, a doublet with one of the doublet peaks hidden by the absorption from the A form. This was done by taking advantage of the fact that the position of the NH signals change with concentration and temperature. In this way the *AB* pattern of the A form could be displaced (changing in position and intensity with the chemical shift difference between the formyl and the NH protons) allowing it to be shown that *H*CON*H* coupling is not present in the B form.

The results obtained from the ^1H NMR spectra of acetyl *N*,*N*-diisopropylhydrazine (II) are listed in Table 2. The relative proportions of the A and the B form were again observed to change characteristically with the solvent.

Table 2. ^{1}H NMR Chemical shifts [a] (τ, ppm), coupling constants (J, Hz) and the magnetic nonequivalence of the isopropyl methyl groups (Δ, Hz) of acetyl N,N-diisopropylhydrazine (II)

IIA IIB

Solvent	Conc. %	Temp. °C	Form (%)	NPr^i_2				CH_3CONH	
				CH_3(2)	Δ	CH(7)	J	CH_3(1)	NH(1)
CCl_4	6	40	A(100)	9.00 8.94	3.7	6.83	6.4	8.04	1.77
$CDCl_3$	8	40	A (85)	9.01 8.92	5.2	6.87	6.5	7.91	3.46
			B (15)	8.94	—	6.84	6.4	8.01	3.83
$CDBr_3$	10	40	A (75)	8.97 8.90	4.9	6.93	6.5	7.90	3.27
			B (25)	8.80	—	6.91	6.5	7.82	—obs
CD_3OD	6	40	A (25)	9.00 8.92	4.9	6.77	6.4	7.93	—
			B (75)	8.98	—	6.82	6.3	8.06	—

[a] See Table 1.

From the close similarity between these data and those discussed above there can be little doubt that the species which occurs in CCl_4 solution is the pure A form, and the species which increases in significance when the dielectric constant of the solvent is raised must be the B form. An additional interesting feature is the occurrence of magnetic nonequivalence of the methyl protons of the diisopropylamino group of the A form. It was found by variable temperature measurements that this nonequivalence persisted in $CDCl_3$, with virtually unaltered value until 55°C, which is near the upper limit of temperature at which this solvent can be used. Measurements in $CDBr_3$ showed the nonequivalence to disappear at approximately 81°C. On the other hand, cooling of the $CDCl_3$ solution failed to produce nonequivalence in the methyl signals from the diisopropylamino groups of the B form even at −40°C, and from Table 1 it can be seen that both A and B forms of (I) are devoid of nonequivalence in the methyl signals at −40°C in $CDCl_3$.

Inspection of molecular models show that the occurrence of nonequivalence in IIA can be explained by the limitations which the methyl moiety of the acetyl group imposes on the steric requirements of the diisopropylamino group. A search in the literature shows that cases of hindered inversion of non-

planar trigonal nitrogen are few[11,12] and rather special in nature. Apparently, in this case, the size of the methyl group bonded to the carbonyl moiety is sufficient to hinder inversion at the nitrogen atom of the diisopropylamino group, with the result that magnetic nonequivalence of the methyl signals of the latter group is produced.

The solvent dependence of the ^{1}H NMR signals of isobutyryl *N*,*N*-diisopropylhydrazine (III) was studied at room temperature (Table 3) and on this

Table 3. ^{1}H NMR Chemical shifts [a] (τ, ppm), coupling constants (*J*, Hz) and the magnetic nonequivalence of the methyl groups (*Δ*, Hz) of isobutyryl *N*,*N*-diisopropylhydrazine (III)

IIIA IIIB

Solvent	Conc. %	Temp. °C	Form (%)	NH(1)	NPr^i_2				Pr^iCO		
					CH_3(2)	*Δ*	CH(7)	*J*	CH_3(2)	CH(7)	*J*
CCl_4	6	40	A(98)	1.84	9.00 8.98	1.2	6.83	6.6	8.94	6.63	6.5
CS_2	6	40	A(98)	2.05	9.00	0	6.93	6.4	8.93	6.71	6.2
$CDCl_3$	10	40	A(50)	4.00	9.01 8.90	5.9	6.93	6.4	8.93	6.64	6.2
			B(50)	4.00	8.96	—	6.89	6.4	8.82	7.75[b]	6.4
CD_3OD	10	40	A(5)	—	8.93 8.91	1.0	—obs	6.6	—obs	—obs	—obs
			B(95)	—	8.98	0	6.82	6.5	8.87	7.45[b]	6.6
$CDBr_3$	10	60	A(65)	3.80	9.00 8.96	2.3	6.92	6.4	8.92	6.70	6.6
			B(35)	3.80	8.92	—	6.89	6.6	8.83	7.62[b]	6.6
		80	A(70)	3.97	8.97	0	6.93	6.4	—obs	6.72	6.6
			B(30)	3.97	8.93	—	6.89	6.6	8.84	7.64[b]	6.6
		100	A(100)	4.02	8.97	0	6.90	6.4	8.90	—obs	6.6

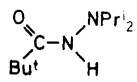
[a] See Table 1.
[b] Second order splitting; data published separately.[21]

basis the ^{1}H NMR signals were assigned to the A and the B forms. From the results discussed above it was expected that the observation of magnetic nonequivalence of the methyl groups of the diisopropylamino group would be

a most useful criterion for the validity of this assignment, and it was therefore positively confirmed, that the nonequivalence of the A form persists beyond 60°C in $CDBr_3$ and that nonequivalence does not develop in the signals from the B form when the $CDCl_3$ solution was cooled to −40°C. So far, although the theory correlated with the experimental facts, the magnetic nonequivalence of the A form is, however, much less than expected in CCl_4 and CH_3OH (1.0—1.2 Hz), and is only observed in CS_2 solution on cooling below 40°C. The reasons for these solvation effects have not been clarified. From the temperature dependence in $CDBr_3$ it is seen that only the A form is observed at temperatures exceeding 100°C.

The results listed in Table 4 for pivaloyl *N*,*N*-diisopropylhydrazine (IV) confirm the assignments given in Tables 1—3. The bulkiness of the *tert*-butyl group prevents formation of the A form in detectable amounts even in

Table 4. ^{1}H NMR Chemical shifts [a] (τ, ppm) and coupling constants (*J*, Hz) of pivaloyl *N*,*N*-diisopropylhydrazine (IV)



IVB

Solvent	Conc. %	Temp. °C	Pr^i_2N			Bu^tCONH	
			CH_3(2)	CH(7)	*J*	CH_3(1)	NH(1)
CCl_4	6	40	9.00	6.83	6.3	8.81	3.95
CS_2	6	40	9.05	6.89	6.3	8.86	3.95
Benzene	6	40	9.05	6.99	6.4	8.88	−obs
$CDCl_3$	10	40	8.96	6.87	6.4	8.75	3.90
		−40	8.92[b]	6.81	6.4	8.71	3.77

[a] See Table 1.
[b] Broad singlet with shoulders at 9.00 and 8.84 ppm.

CCl_4 although this solvent was expected to favour this form. From the arguments given above it can be expected that the methyl signals from the diisopropylamino group should be equivalent in the B form in the temperature range down to −40°C. This is essentially confirmed since it appears from the table that the nonequivalence just begins to appear at this temperature in the form of a broadening of the signals.

When the ^{1}H NMR spectra of the corresponding thioacyl *N*,*N*-diisopropylhydrazines were investigated it was found that solutions of thioacetyl and

Table 5. ^{1}H NMR Chemical shifts [a] (τ, ppm), coupling constants (J, Hz) and the magnetic nonequivalence of the isopropyl methyl groups (Δ, Hz) of thioacyl N,N-diisopropylhydrazines (V—VII)

A C

R	Solv.	Conc. %	Temp. °C	Form (%)	NPr$^i_2$					R	NH	J_{RNH}
					CH_3(2)	Δ	CH(7)	J_{CHCH_3}	J_{CHNH}			
H(V)	CCl_4	16	40	A(97)	8.94	0	6.71	6.2	0	1.03(2)	0.40(2)	12.2
fresh solutions	$CDCl_3$	6	40	A(97)	8.93	0	6.79	6.4	0	0.78(2)	1.57(2)	13.1
			−40	A(90)	8.91	0	6.70	6.4	0	0.72(2)	0.17(2)	13.0
				C(10)	8.60	4.1	6.18	6.6	ca. 4	0.55(1)	−obs	0
					8.53		6.11					
		16	−40	A(93)	8.93	0	6.68	6.2	0	0.72(2)	−0.16(2)	13.0
				C(7)	8.63	4.4	6.07	6.6	4.6	0.54(1)	−obs	0
					8.52		6.00					
	CD_3OD	16	40	A(95)	8.97	0	6.75	6.4	0	0.90(1)	−obs	−obs
H(V) aged two weeks	$CDCl_3$	16	40	A(76)	8.96	0	6.77	6.4	0	0.85(1)	−obs	−obs
				C(24)	8.63	0	6.27	6.4	5.0	0.73(1)	−obs	0
							6.19					
CH_3(VI)	CCl_4	6	40	A(96)	8.93	1.9	6.71	6.3	0	7.47(1)	0.63(1)	0
					8.90							
				C(4)	8.66	0	−obs	6.1	−obs	7.66(1)	−obs	0
	CD_3OD	6	40	A(94)	8.97	2.8	6.68	6.4	0	7.44(1)	−obs	0
					8.93							
				C(6)	8.73	0	−obs	6.4	−obs	7.58(1)	−obs	0
	$CDCl_3$	10	40	A(93)	8.95	1.4	6.75	6.4	0	7.42(1)	1.40(1)	0
					8.92							
				C(7)	8.62	0	6.41	6.6	5.0	7.55(1)	−obs	0
							6.33					
			−40	A(93)	8.94	3.0	6.65	6.5	0	7.35(1)	0.32(1)	0
					8.89							
				C(7)	8.61	4.2	−obs	6.6	−obs	7.46(1)	−0.52(1)	0
					8.54							
	$CDBr_3$	11	40	A(90)	8.90	0	6.74	6.4	0	7.43(1)	1.63(1)	0
				C(10)	8.63	0	−obs	6.6	−obs	7.40(1)	−0.70(1)	0
$(CH_3)_3C$ (VII)	$CDCl_3$	6	40	C(100)	8.66	0	6.36	6.6	5.0	8.70(1)	−1.30(1)	0
							6.28					
			−40	C(100)	8.68	3.6	6.24	6.4	5.8	8.72(1)	−1.40(1)	0
					8.62		6.15					

[a] See Table 1.

thiopivaloyl *N*,*N*-diisopropylhydrazine (VI and VII, respectively) were almost unchanged with time. In contrast, thioformyl *N*,*N*-diisopropylhydrazine (V) slowly rearranged from the nonpolar A form to the dipolar structure-C. The results and formulas for the species in equilibrium are summarized in Table 5. The situation, with respect of our knowledge of the equilibrium between dipolar and nonpolar forms of related compounds, is very unsatisfactory. Investigations of ten thiocarbazoylimidazoles [4] have shown that they are exclusively dipolar (structure C of Table 5 with R=imidazole), monomeric in solution and polymeric in the solid phase. A ^{1}H NMR investigation of dithiocarbazic esters [13] shows an equilibrium between form A and form C in solution (Table 5, R=*S*-alkyl or *S*-aryl). Furthermore, a rough correlation seems to exist between the bulkiness of R and the amount of C present in the equilibrium mixture. For example, *tert*-butyl *N*,*N*-diisopropyldithiocarbazate is almost exclusively present as the dipolar form C, which is readily identified by the coupling between the NH proton and the CH protons of the isopropyl groups. The form of acylhydrazines, corresponding to the B form discussed above, has been observed in the case of *O*-phenyl *N*,*N*-diisopropylmonothiocarbazate,[14] which contains A, B, and C forms in equilibrium. Probably a B form is also present in some special thiocarbonohydrazides (see below). Finally, a tautomeric thiol form of thiocarbonylhydrazines has apparently never been reported, but its presence has been established in this laboratory [15] in the case of thiobenzoylhydrazines with an *ortho* substituent capable of forming hydrogen bonds.

The ^{1}H NMR spectral data of thioformyl *N*,*N*-diisopropylhydrazine (V) in different solvents (Table 5) showed that only small variations in the ratio of A form to C form occurred in fresh solutions. The solutions were then allowed to stand until the ^{1}H NMR spectra were unchanged with time. In solutions of CCl_4, $CDCl_3$ and CH_3OH, where equilibrium had apparently been obtained, the amounts of A form were 88 %, 76 %, and 82 %, respectively. The conclusion mentioned above, that the equilibrium between A and B forms for acylhydrazines is displaced towards the B form when the dielectric constant of the solvent is raised, has therefore no obvious parallel in the case of the equilibrium between the A and C forms observed by thioacylhydrazines.

An identification of the nonpolar forms of V and VI as A forms (Table 5), *i.e.* with the NH proton *cis* to the thiocarbonyl group, was based on the following evidence: (1) The coupling of the thioformyl proton to the NH proton in V was found to be in the range 12—13 Hz, and somewhat dependent on the solvent. This is typical of a *trans* coupling constant and close to the value found for the oxygen analogue (I). A similar criterion was applied to thioformanilide by Rae [16] who argued that the coupling constant (14.8 Hz) was only compatible with a *trans* structure. (2) An A form was not observed in the case of thiopivaloyl *N*,*N*-diisopropylhydrazine (VII). This is again analogous to the results obtained with the pivaloyl compound IV and in line with expectations based on similar steric arguments. (3) Magnetic nonequivalence was observed to occur in the isopropyl methyl signals from the A form of VI but not in the corresponding signals of V. This is an exact parallel to the observations on I and II discussed above. Furthermore, it is a necessary corollary to the

explanation suggested, *i.e.* hindered inversion of the nitrogen atom of the diisopropylamino group by the methyl group.

It was noted that the nonequivalence of VI disappeared at a lower temperature than that of II. A solution of VI in $CDBr_3$ only displayed nonequivalence when it was cooled below 40°C, whilst a solution of II in $CDBr_3$ showed nonequivalent methyl signals up to 81°C. The result, that substitution of oxygen with sulfur raises the temperature limit for nonequivalence by *ca.* 40°C, cannot at present be satisfactory explained. In $CDCl_3$ the corresponding temperature at which nonequivalence disappeared for VI was 41°C, while the nonequivalence for II remained unchanged up to the boiling point of the solution; the effect, therefore, is not only due to the solvent.

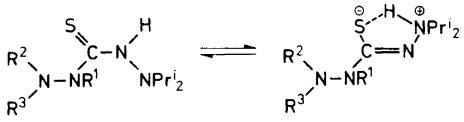
The infrared spectrum of thiopivaloyl *N*,*N*-diisopropylhydrazine (VII) recorded in KBr or in solution was quite different from the infrared spectra of the other thioacyl *N*,*N*-diisopropylhydrazines. A typical infrared spectrum of the nonpolar form has a sharp, strong NH stretching band above 3000 cm^{-1} and a very strong, somewhat broad band between 1500 and 1600 cm^{-1} due to the thioureide grouping.[17] The characteristics of the dipolar C form have been discussed before [4] and also apply to the infrared spectrum of VII: a broad band of medium strength around 2500 cm^{-1} with several submaxima originating from NH stretching vibration, and a very strong band near 1460 cm^{-1}, mainly due to the C=N stretching motion.

The identification of the C form by the ^1H NMR spectra was unambiguous in the cases where a coupling could be observed between the NH and the methine protons of the isopropyl groups and was substantiated by spin decoupling or shaking with deuterium oxide. The ^1H NMR characteristics of dipolar structures have been discussed in detail previously [4] and are all also observed in the present case. For diagnostic purposes the following observations are of interest: (1) the shift of the methyl signals of the isopropyl group towards lower field (from *ca.* $\tau = 8.9-9.0$ ppm to the region $\tau = 8.5-8.7$ ppm), (2) the shift of the methine septuplet of the same group towards lower field (from the region $\tau = 6.6-6.8$ ppm to $\tau = 6.1-6.4$ ppm), and (3) the appearance of nonequivalence of the methyl doublet of the isopropyl group at slightly lower temperature.

The latter phenomenon deserves a special comment. Nonequivalence of the isopropyl methyl signals of the C forms of imidazolides [4] did not disappear on heating until temperatures in the range 60—80°C had been reached. Even at this temperature the C*H*—N*H* coupling was still present, and the final rationalization of these results resulted in a model in which this coupling is a necessary prerequisite for nonequivalence to occur. Nonequivalence of the dipolar C forms of V, VI, and VII did not occur above *ca.* 40°C, 30°C, and 23°C, respectively. This observation is in accord with the proposed model [4] since introduction of the electron-releasing alkyl groups instead of the electron-attracting imidazole group is expected to raise the base strength of the thiocarbonyl sulfur and thereby facilitate inversion at the nitrogen atom carrying the isopropyl groups. Furthermore, in support of the proposed model, N*H*—C*H* coupling was observed in V—VII at temperatures above the disappearance temperature of nonequivalence.

A variation in the isomer ratio with the steric requirement of the group connected to the thiocarbonyl group has also been established from ^{1}H NMR spectra of thiosemicarbazides and thiocarbonohydrazides. The first class of compound will be the subject of some forthcoming publications from this laboratory [15,18] and it will be sufficient to mention here that 15 differently substituted 1,1-diisopropylthiosemicarbazides have been shown to occur in $CDCl_3$ solution mainly in the A form (with nonequivalence of the isopropyl

Table 6. ^{1}H NMR signals at 40°C of the diisopropylamino group [a] (τ, ppm) of 5–10 % solutions of 1,1-diisopropylthiocarbonohydrazides substituted in the 4- and in the 5-positions.



A C

R^1	R^2	R^3	Solvent	Form %	CH_3(2)	CH(7)
H	H	phenyl	DMSO-d_6	A(100)	8.96 8.87	6.84
H	H	cyclohexyl	$CDCl_3$	A(100)	9.01 8.94	6.89
H	H	benzoyl	$CDCl_3$	A(100)	8.94 8.85	6.84
H	H	phenacetyl	$CDCl_3$	A(100)	8.99 8.92	6.92
H	H	*p*-nitrobenzoyl	$CDCl_3$	A(100)	8.94 8.83	6.84
H	H	*p*-toluenesulfonyl	$CDCl_3$	A(100)	9.09 8.96	6.96
H	H	*N*,*N*-dimethylthio-carbaminoyl	$CDCl_3$	A(100)	8.96 8.85	6.87
H	H	*N*,*N*-diisopropylthio-carbazoyl	$CDCl_3$	A(100)	8.95 8.86	6.87
H	CH_3	ethylthio-thiocarbonyl	$CDCl_3$	A(100)	8.91 8.85	6.73
H	CH_3	*N*,*N*-dimethylthiocarbazoyl	$CDCl_3$	A(89)	8.96 8.90	6.75
				C(11)	8.71 8.62	—obs
H	$-CH_2-CH_2-O-CO-$		$CDCl_3$	A(97)	8.95 8.88	6.86
				C(3)	8.70 8.63	—obs
CH_3	H	H	$CDBr_3$	B(100)	8.81	6.59

[a] See Table 1.

methyl signals) but in some instances (4,4-disubstituted compounds, including 4,4-disubstituted 1,1-diisopropylselenosemicarbazides) also in a dipolar form analogous to the C form discussed here. Some results obtained from the ^{1}H NMR spectra of 1,1-diisopropylthiocarbonohydrazides are listed in Table 6 for comparison. It was anticipated, that as long as the 4-substituent R^1=H they would occur mainly in the A form, possibly in equilibrium with small amounts of C form. This is borne out by the experimental data which show that if just one of the 5-substituents is different from hydrogen the group becomes sufficiently bulky to induce conversion to the C form.

An interesting exception is 4-methyl-1,1-diisopropylthiocarbonohydrazide in which nonequivalence was not observed even by cooling the solution to the crystallization point close to 0°C. Since the space-filling properties of the NH_2—$N(CH_3)$-group roughly correspond to those of an isopropyl group this result cannot really be explained except by assuming the group to be situated in *trans*-position to the diisopropylamino group. Accordingly, this compound has been assigned the B form.

EXPERIMENTAL

Conditions and equipment used for the physical measurements have been summarized in an earlier paper.[19] Almost all the compounds used in this investigation have been prepared from isothiocyanatodiisopropylamine [1-3] and were analytically pure. Formyl and thioformyl *N,N*-diisopropylhydrazine were prepared by the method described by Bredereck *et al.*[20] and their identity confirmed by m.p. and elemental analysis.

Acetyl N,N-*diisopropylhydrazine (II).* A solution of 1,1-diisopropylhydrazine (0.1 mol) and acetic acid anhydride (0.1 mol) in benzene (20 ml) was boiled for 1 h. The benzene solution was evaporated to dryness and the crystalline residue was recrystallized twice from pentane. Yield 40 % of acetyl *N,N*-diisopropylhydrazine, m.p. 82—83°C. (Found: C 60.62; H 11.32; N 17.46. Calc. for $C_8H_{18}N_2O$: C 60.72; H 11.46; N 17.71).

Isobutyryl N,N-*diisopropylhydrazine (III).* Isobutyryl chloride (0.1 mol), dissolved in dry ether (20 ml), was slowly added to solution of diisopropylhydrazine (0.2 mol), also in dry ether (50 ml). The reaction mixture was left at room temperature for 24 h. After filtering off the separated diisopropylhydrazinium chloride the solvent was evaporated. The residue was recrystallized from pentane to give 1.3 g isobutyryl *N,N*-diisopropylhydrazine (70 %), m.p. 144—145°C. (Found: C 64.25; H 11.92; N 14.96. Calc. for $C_{10}H_{22}N_2O$: C 64.47; H 11.90; N 15.04).

Pivaloyl N,N-*diisopropylhydrazine (IV).* This compound was prepared from pivaloylchloride and diisopropylhydrazine following the procedure given above for (III). The yield was 45 % of colourless crystals, m.p. 134—135°C. (Found: C 65.78; H 12.10; N 13.78. Calc. for $C_{11}H_{24}N_2O$: C 65.95; H 12.08; N 13.99).

The two following compounds were prepared in cooperation with Dr. H. Mygind.

Thioacetyl N,N-*diisopropylhydrazine (VI).* 1,1-Diisopropylhydrazine (2.0 g) was added to a solution of methyl dithioacetate (1.7 g) in methanol (10 ml) and the resultant solution allowed to stand for three days at room temperature. The methanol was removed in vacuum and the residue extracted with ligroin (b.p. 60—90°C). The extract was filtered and the solvent removed to give a crystalline residue. Repeated recrystallizations from pentane, using active carbon, finally afforded 23 % of a colourless, crystalline compound, m.p. 60.5—61.5°C. (Found: C 55.05; H 10.63; N 16.38. Calc. for $C_8H_{18}N_2S$: C 55.12; H 10.41; N 16.08).

Thiopivaloyl N,N-*diisopropylhydrazine (VII).* A suspension of phosphorus pentasulfide (3.0 g), in a solution of pivaloyl *N,N*-diisopropylhydrazine (3.0 g) in benzene (50 ml), was kept at reflux temperature with stirring for 6 h. After cooling the mixture was filtered and the remnants washed several times with benzene. Evaporation of the benzene left an yellow oil containing a few crystals. This was purified by PLC. Elution with a mixture of methanol, ether, and chloroform (4:3:3) gave a series of fractions, of which only the second (measured from the front) gave IR and ^{1}H NMR spectra consistent

with those expected for VII. This fraction was again separated in a series of fractions by elution with a mixture of equal amounts of benzene and petrol ether. The fraction closest to the base line consisted of pure VII, which was recrystallized from pentane. The yield was 1 % (35 mg) of a colourless crystalline compound with a m.p. of 42—44°C. (Found: 61.01; H 11.17; N 12.84. Calc. for $C_{11}H_{24}N_2S$: C 61.05; H 11.18; N 12.95).

Note added in proof. The isomerism between nonpolar and dipolar forms of thioformyl *N,N*-diethylhydrazine has been described in a separate communication.[22] We regret to have overlooked an earlier paper by Walter and Reubke [23] discussing the same subject.

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