231. Reactions of 2-Diisopropylamino-3,7-dehydrotropone[1]): Conversion to the Thione and Dimerization

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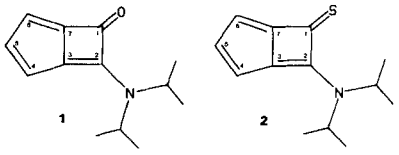
Reaktionen von 2-Diisopropylamino-3,7-dehydrotropon: Umwandlung in das Thion und Dimerisierung

Zusammenfassung

Behandlung von 2-Diisopropylamino-3,7-dehydrotropon (**1**) mit Phosphorpentasulfid ergab 2-Diisopropylamino-3,7-dehydrotropothion (**2**). Mit Trifluoressigsäure entstand aus **1** ein stabiles Dimeres (**5**), das ein Dehydrotropon- sowie ein Tropon-Ringsystem enthält. Die Strukturen von **2** und **5** ergeben sich aus ihren Spektraleigenschaften.

In continuance of our studies on the dehydrotropone system [1–3], we examined the behaviour of 2-diisopropylamino-3,7-dehydrotropone (**1**)[2]) under two conditions: 1) with phosphorus pentasulfide, which led to the first example of a 3,7-dehydrotropothione, and 2) with trifluoroacetic acid, which induced a dimerization involving an unusual 3,7-dehydrotropone → tropone ring opening.

1. 2-Diisopropylamino-3,7-dehydrotropothione (2)[3]). – Treatment of 2-diisopropylamino-3,7-dehydrotropone (**1**) [1] with phosphorus pentasulfide and triethylamine at room temperature in dichloromethane (compare [4]) for 9 days caused simple replacement of the O- by a S-atom to yield 2-diisopropylamino-3,7-dehydrotropothione (**2**) as an orange solid, m.p. 105–106°. Its spectral properties, shown in *Table 1* together with those of **1**, offer structural confirmation as follows:



1 2

[1]) In accordance with the previous literature [1–4], we prefer to use the dehydrotropone and the tropone nomenclature throughout this paper, rather than the systematic nomenclature, which is given in footnotes 2, 3 and 5.

[2]) The systematic name for **1** is 7-diisopropylamino-bicyclo[3.2.0]-1(7),2,4-heptatrien-6-one.

[3]) The systematic name for **2** is 7-diisopropylamino-bicyclo[3.2.0]-1(7),2,4-heptatriene-6-thione.

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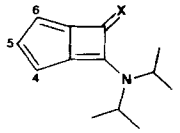
Table 1. *Comparison of some spectral properties*[a]) *of 2-diisopropylamino-3,7-dehydrotropone* (**1**) *and 2-diisopropylamino-3,7-dehydrotropothione* (**2**)



				1 (X=O) [1]	**2** (X=S)
UV. (C_2H_5OH)					251 (12000)
				252 (33100) [1]	285 (31500)
				304 (14000)	348 (15500)
				345–355 (1200)	406 (2500)
IR. ($CHCl_3$)				1730*vs* [1]	1655*vs*
				1630*vs*	1145*m*
^{1}H-NMR. (CCl_4)	$CH(CH_3)_2$	*syn*[b])	CH	5.03 (*sept.*, J=6.5, 1 H)	6.70 (*sept.*, J=6.7)
			CH_3	1.40 (*d*, J=6.5, 6 H)	1.34 (*d*, J=6.7)
		anti	CH	3.84 (*sept.*, J=6.5, 1 H)	3.84 (*sept.*, J=6.7)
			CH_3	1.55 (*d*, J=6.5, 6 H)	1.52 (*d*, J=6.7)
	H–C(4)			6.25 (*d*, J=3.6, 1 H)	6.38 (*d*, J=3.2)
	H–C(6)			6.20 (*d*, J=3.2, 1 H)	6.19 (*d*, J=3.2)
	H–C(5)			7.32 (*d*×*d*, J=3.6 and 3.2, 1 H)	7.33 (*d*×*d*, J=3.2 and 3.2)

[a]) The numerical values for the UV. spectra are in nm (ε), for the IR. spectra in cm^{-1} and for the ^{1}H-NMR. spectra (60 MHz for **1** and 90 MHz for **2**) as δ in ppm and J in Hz.

[b]) See footnote 4.

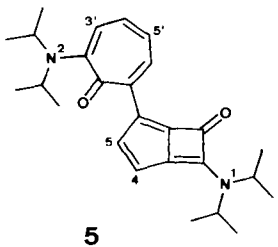
The two longest wavelength UV.-maxima of **2** are bathochromically shifted by $\Delta\lambda = 44$ to 56 nm as compared to the corresponding ones of **1**. These shifts and the increase in intensities have their analogy in the comparison of tropothione and two of its derivatives with tropone and the corresponding derivatives ($\Delta\lambda = 46$ to 70 nm), a comparison which has been summarized in [4].

The IR. spectra of **1** and **2** differ characteristically in the 1550–1800 cm^{-1} range, where **1** shows two bands, the thione **2**, however, only one. In the region of the (C=S)-absorption (given in [5] as 1050–1200 cm^{-1}) the thione **2** has a relatively sharp band at 1145 cm^{-1}.

The ^{1}H-NMR. spectra of **1** and **2** are very similar as far as the twelve methyl protons of the two isopropyl groups, the three olefinic protons H–C(4), H–C(5) and H–C(6) and the methine proton of the *anti*-isopropyl group[4]) are concerned. But a large difference is shown in the chemical shift of the *syn*-isopropyl methine proton, which is identified in **1** and in **2** by the fact that it is shifted downfield with respect to the corresponding *anti*-proton ($\delta = 3.84$ ppm) because of its proximity to the (C=X)-functionality (X=O or S). The further downfield shift of this *syn*-proton ($\delta = 6.70$ ppm) in **2**, as compared to that in **1** ($\delta = 5.03$ ppm), must be due to the stronger anisotropic deshielding effect of the (C=S)-than of the (C=O)-group [6]. It is of interest to note that the rotation around the C(2),N-bond in **2** is slow on

[4]) *Syn* and *anti* refer to the position of an isopropyl group relative to the carbonyl group.

Table 2. *Some IR. bands and ^{1}H-NMR. signals of 2-diisopropylamino-6-(2′-diisopropylaminotropon-7′-yl)-3, 7-dehydrotropone* (**5**), *2-diisopropylamino-3, 7-dehydrotropone* (**1**) *and 2-dimethylaminotropone* (**3**)[a])



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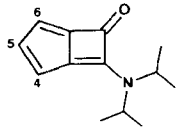

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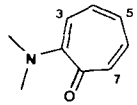

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IR. ($CHCl_3$)			1730*vs* 1635*vs* 1570*m*	1730*vs* 1630*vs*	1580*m* 1580*sh* 1556*vs*
^{1}H-NMR. ($CDCl_3$)					
H–C(5)			8.07 (*d*, *J* = 3.6, 1 H)	7.51 (*d* × *d*, *J* = 3.6 and 3.2, 1 H)	–
H–C(4)[b])			6.48 (*d*, *J* = 3.6, 1 H)	6.48 (*d*, *J* = 3.6, 1 H)	–
H–C(6)			–	6.40 (*d*, *J* = 3.2, 1 H)	–
$(CH_3)_2CH$–N–C(2)	*syn*[c])	CH	5.22 (*sept.*, *J* = 6.6, 1 H)	5.25 (*sept.*, *J* = 6.5, 1 H)	–
		CH_3	1.42 (*d*, *J* = 6.6, 6 H)	1.45 (*d*, *J* = 6.5, 6 H)	–
	anti[c])	CH	4.00 (*sept.*, *J* = 6.6, 1 H)	3.99 (*sept.*, *J* = 6.5, 1 H)	–
		CH_3	1.51 (*d*, *J* = 6.6, 6 H)	1.55 (*d*, *J* = 6.5, 6 H)	–
$(CH_3)_2CH$–N–C(2′)		CH	4.00 (*sept.*, *J* = 6.6, 2 H)	–	
		CH_3	1.34 (*d*, *J* = 6.6, 12 H)	–	
N–CH_3			–	–	3.02 (*s*, 6 H)
H–C(3′)[b])			6.55 (*d*, *J* = 10.2, 1 H)	–	6.43 (*d*, *J* = 10.1, 1 H)
H–C(4′)[b])			6.68 (*d* × *d*, *J* = 10.2 and 10.2, 1 H)	–	6.95 (*d* × *d* × *d*, *J* = 10.1, 10.1 and 1.0, 1 H)
H–C(5′)			6.47 (*d* × *d*, *J* = 9.3 and 10.2, 1 H)	–	6.49 (*d* × *d*, *J* = 10.1 and 8.0, 1 H)
H–C(6′)[b])			7.70 (*d*, *J* = 9.3, 1 H)	–	7.00 (*d* × *d* × *d*, *J* = 11.5, 8.0 and 1.0, 1 H)
H–C(7′)			–	–	6.86 (*d*, *J* = 11.5, 1 H)

[a]) The numerical values for the IR. spectra are in cm^{-1} and for the ^{1}H NMR. spectra as δ in ppm and *J* in Hz.

[b]) These H-atoms are replaced by ^{2}H-atoms in [$^2H_4$]-**5**.

[c]) For the meaning of *syn* and *anti* refer to footnote 4.

the ^{1}H-NMR. time scale at room temperature, just as it is in **1** [1]; this implies that the push-pull delocalization involving a (C=S)-group is similar to the one involving a (C=O)-group.

2. 2-Diisopropylamino-6-(2′-diisopropylaminotropon-7′-yl)-3,7-dehydrotropone (5)[5]. – On attempting to measure the ^{1}H-NMR. spectrum of 2-diisopropylamino-3,7-dehydrotropone (**1**) in CF_3COOH solution, we observed the occurrence of a slow reaction. After five days a stable product **A** could be isolated as orange-red platelets. The arguments for assigning a structure to this product are as follows[6]):

$$\mathbf{1}\ (C_{13}H_{17}NO) \xrightarrow{CF_3COOH} \mathbf{A}\ (C_{26}H_{34}N_2O_2)$$

The dimeric nature of **A** is evident from the highest mass peak at 406 *m/z* in the mass spectrum. A more extended conjugation, as compared to that of **1**, manifests itself in the UV. absorptions at 403 and 465 nm. The two portions of the dimer **A**, each derived from a molecule of **1**, will be called moieties 1 and 2. In order to derive structure **5** for the dimer **A** we draw attention to the following features (see *Table 2*) of the IR. and especially the 360-MHz-^{1}H-NMR. spectra in comparison with the corresponding ones of two model compounds, namely of the starting material 2-diisopropylamino-3,7-dehydrotropone (**1**) and of 2-dimethylaminotropone (**3**), synthesized according to [7][7]).

That certain structural aspects of the starting material **1** are still present in **A** can be recognized in the unchanged intensity ratio (14:3) of the two groups of ^{1}H-NMR. signals of **A**, the one at higher field (in the ranges of 5.22 to 4.00, 4 H, and of 1.51 to 1.34 ppm, 24 H), due to the isopropyl groups, and the one at lower field (in the range of 6.47 to 8.07 ppm, 6 H), due to the olefinic protons. The structural change which had occurred during dimerization is signalled by the (dynamic) homotopicity of two (of the four) isopropyl groups (shown by the doublet at $\delta = 1.34$ ppm, 12 H) and by the two separate proton coupling systems, one an *AB*- ($J = 3.6$) and the other a *CDEF*-system ($J_{CD} = 10.2$, $J_{DE} = 10.2$ and $J_{EF} = 9.3$ Hz). The *AB*-system with its small coupling constant and its low field signal ($\delta = 8.07$ ppm), the signals of the two heterotopic isopropyl groups ($\delta = 5.22$ and 4.00/both septets, $\delta = 1.51$ and 1.42/both doublets) and the IR. bands at 1730 and 1635 cm^{-1} are so reminiscent of **1** that we conclude moiety 1 to have retained its 2-diisopropylamino-3,7-dehydrotropone skeleton. However, one olefinic H-atom of **1** is missing

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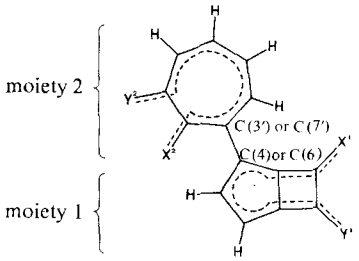
[5]) The systematic name for **5** is 4-(3′-diisopropylamino-2′-oxo-cyclohepta-3′,5′,7′(1′)-trien-1′-yl)-7-diisopropylamino-bicyclo[3.2.0]-1(7),2,4-heptatrien-6-one. Note that our numbering of the C-atoms of **5** does not correspond to this systematic name, but – for the sake of the discussion on the structure derivation – rather to each of the two ring systems contained in **5**, where the O-atom and the amino substituent mark positions 1 and 2, respectively.

[6]) First experiments to obtain an X-ray structural analysis of **A**, undertaken by Dr. *R. Grieb* at the Institut für Kristallographie und Petrographie at the ETH Zürich, encountered difficulties probably due to crystal quality. Dr. *Grieb*'s untimely death prevented completion of these experiments.

[7]) An attempt to prepare 2-diisopropylaminotropone by the method described for **3** in [7] was unsuccessful.

in **A** and the *J*-value of the *AB*-system (3.6 Hz) shows that it cannot be the original H–C(5). It follows that moiety 1 carries a substituent (moiety 2) at the original C(4) or C(6). The olefinic H-atom missing in moiety 1 has evidently moved to moiety 2, because the latter now has four olefinic H-atoms (instead of the three from **1**), the ones of the *CDEF*-system. To accomodate this new H-atom, a bond must have been broken in **1** during its transformation to moiety 2. Since the coupling pattern of the *CDEF*-system of **A** shows that the four olefinic protons of moiety 2 constitute a sequence of vicinal neighbours, the new H-atom must have placed itself on what in **1** was C(3) or C(7). The coupling constants (10.2, 10.2 and 9.3 Hz) within the *CDEF*-system exclude a 5-membered ring as the skeleton for the four olefinic H-atoms, so that the broken bond must have been the one between the original C(3) and C(7), leaving one of these two centres as the point at which moiety 1 attached itself to moiety 2. It follows that moiety 2 is the result of a conversion of **1** to a tropone system. This is confirmed by the similarity (see *Table 2*) of all its ^{1}H-NMR. features (the *CDEF*-system and the isochronous *N*-alkyl groups) as well as the IR.-band at 1570 cm^{-1} with the corresponding features of 2-dimethylaminotropone (**3**) (see also section 3).

The preceding arguments led to conclusions on the ring systems (dehydrotropone and tropone) as well as on four attachment alternatives of moieties 1 and 2 in **A**. Formula **4** summarizes the four structures which remain as possibilities.



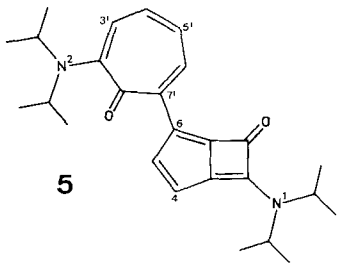
4 X^1, X^2 = O or $N(CH(CH_3)_2)_2$
Y^1, Y^2 = $N(CH(CH_3)_2)_2$ or O

(the isopropyl groups of moiety 2 are homotopic, those of moiety 1 are not)

Further evidence is obtained from nuclear *Overhauser*-^{1}H-NMR. experiments: Irradiation of the twelve (isochronous) methyl protons ($\delta = 1.34$ ppm) enhanced the signal of one of the protons in the *CDEF*-system (namely H–C(3'), $\delta = 6.55$ ppm) by 18%. Thus the diisopropylamino group of moiety 2 is vicinal to an olefinic H-atom and moiety 2 must be substituted at C(7'). A similar experiment with moiety 1 first required identification of the methyl groups belonging to the isopropyl group situated *anti* to the carbonyl group. Clearly the methine proton of this *anti*-isopropyl group is the one at higher field ($\delta = 4.00$ ppm). Decoupling experiments assigned the signal at $\delta = 1.51$ ppm to its geminal methyl groups. Irradiation of these methyl protons ($\delta = 1.51$ ppm) enhanced (by about 18%) the doublet at $\delta = 6.48$ ppm which can be recognized as belonging to moiety 1 by its coupling

constant (3.6 Hz). Thus the C-atom of moiety 1 which is close to the diisopropylamino group, namely C(4), carries a H-atom and moiety 1 must be substituted at C(6).

In accordance with this conclusion we find the chemical shift of H–C(4) ($\delta = 6.48$ ppm) and its coupling constant with H–C(5) ($J = 3.6$ Hz) to be the same in both the monomer **1** and the dimer **5**; furthermore, the signals for the anisochronous *N*-isopropyl groups in **1** and **5** are also practically the same, which would hardly have been expected if the diisopropylamino group of moiety 1 in **5** had been closer to moiety 2. The downfield shift effected by the proximity of the unsaturated ring substituent is demonstrated by the chemical shift of H–C(5) ($\delta = 8.07$ ppm) and of H–C(6′) ($\delta = 7.70$ ppm), as compared to that of the corresponding protons in the model compounds **1** and **3** ($\delta = 7.51$ and 7.00 ppm, respectively). All this establishes structure **5** for the dimer **A**.



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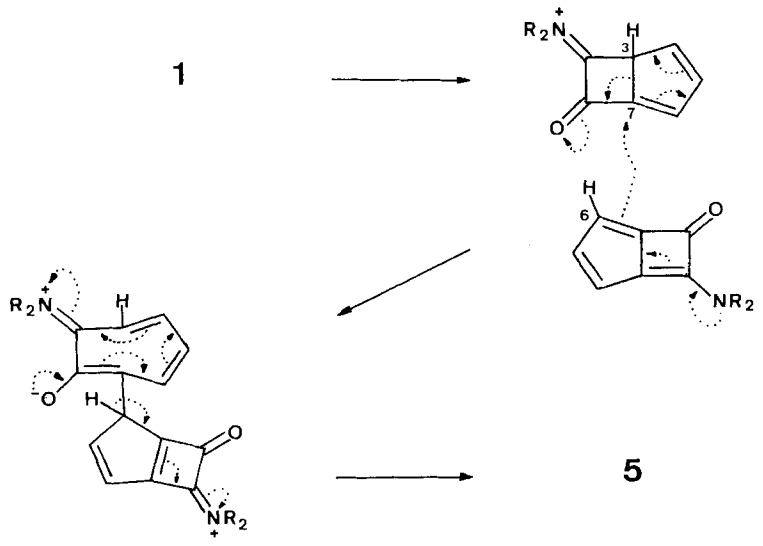
A plausible dimerization mechanism can be formulated, which is illustrated in *Scheme 1* for the formation of **5**. It begins with protonation of **1** at C(3), this being

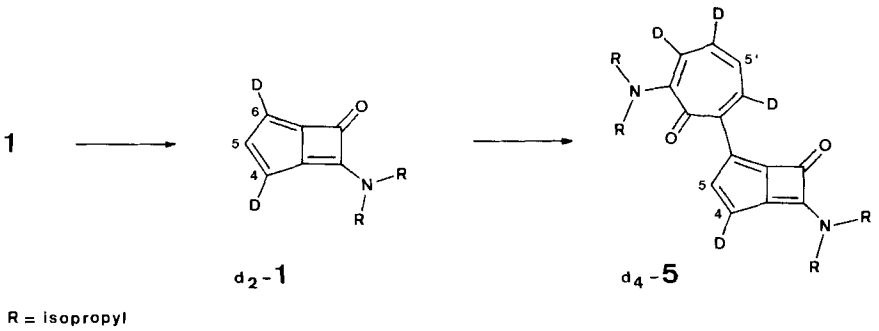
Scheme 1



the most electronegative C-atom according to a calculated charge distribution[8]). The connection between the two moieties is made by the attack of C(6) of a second molecule of **1** at C(7) of protonated **1**, whereby the C(7),C(3)-bond of the latter is broken. Finally deprotonation occurs to **5**.

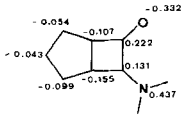
When **1** was treated with deuteriotrifluoroacetic acid a deuteriated dimer [$^2H_4$]-**5** was formed, its mass spectrum indicating the incorporation of four ^{2}H-atoms (M^+ 410 *m/z*). From the ^{1}H-NMR. spectrum (two singlets at 8.07 and 6.47 ppm) it is evident that only two olefinic H-atoms remain in [$^2H_4$]-**5**, namely H–C(5) and H–C(5′) (see *Table 2*). We rationalize the formation of [$^2H_4$]-**5** as follows (see *Scheme 2*): Rapid protolysis reactions in CF_3COOD should effect a selective deuterium exchange of those protons in **1** which sit on C-atoms with relatively high electron density, namely C(4) and C(6)[8]) (see also [2]). Thus the first product in a CF_3COOD solution of **1** should be [4,6-$^2H_2$]-2-diisopropylamino-3,7-dehydrotropone ([$^2H_2$]-**1**). According to the dimerization mechanism proposed in *Scheme 1*, a further ^{2}H-atom is introduced at C(3) of one dimerization partner and another ^{2}H-atom is lost later from C(6) of the other partner. These transformations lead to the structure [$^2H_4$]-**5**, where only two olefinic C-atoms (C(5) and C(5′)) still carry H-atoms, namely those which are derived from the less electronegative C(5) of **1**.

Scheme 2



3. The ^{1}H-NMR. spectrum of 2-dimethylaminotropone (3). – Since, to our knowledge, the ^{1}H-NMR. spectrum of **3** has not been reported a detailed analysis of its 360-MHz-^{1}H-NMR. spectrum was undertaken (see *Table 2*). Assignment of the only two doublets at 6.43 (J = 10.1) and 6.86 ppm (J = 11.5 Hz) to either H–C(3) or H–C(7) enables the sequential characterization of the remaining olefinic proton signals but does not allow unequivocal differentiation between H–C(3) and H–C(7). By irradiating at the six-proton singlet at 3.02 ppm for the methyl groups,

[8]) We thank Prof. *G. Wagniere* and Dr. *J. Kuhn* for communicating to us the results of semi-empirical calculations of the charge distribution of **1**, as follows:



an NOE-enhancement (10%) of the doublet at 6.43 ppm was observed. Hence this signal must be due to H–C(3). Evidently, the dialkylamino substituent exerts an upfield shift on the vicinally located proton. This result is in agreement with the reported ^{1}H-NMR. spectrum for an analogous compound, namely 2-methoxytropone [8], where the higher field doublets is also assigned to H–C(3).

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Experimental Part

For generalities and abbreviations see [9].

2-Diisopropylamino-3,7-dehydrothiotropone (**2**). To 0.53 g (2.61 mmol) 2-diisopropylamino-3,7-dehydrotropone (**1**) and 0.6 g (2.7 mmol) P_2S_5 in 15 ml CH_2Cl_2 was added with stirring 0.75 ml (5.4 mmol) triethylamine. The initially formed pale yellow solution, which slowly darkened, was allowed to stand at RT. for 9 days, then passed through a silica gel column (60 g) eluting with $CHCl_3$. Collection of the front-running deeply yellow band gave 55 mg (10%) of pure **2** as an orange-yellow solid, m.p. 105–106° after recrystallization from hexane at −25°. – UV. (C_2H_5OH): 251 (12000); 285 (31500); 348 (15500); 406 (2500). – IR. ($CHCl_3$): 1655*s*, 1490*m*, 1342*s*, 1295*s*, 1145*m* (C=S). – ^{1}H-NMR. (90 MHz, CCl_4): 7.33 (*d*×*d*, *J* = 3.2 and 3.2, 1H, H–C(5)); 6.70 (*sept.*, *J* = 6.7, 1H, H_{syn}–C(N))[4]; 6.38 (*d*, *J* = 3.2, 1H, H–C(4) or H–C(6)); 6.19 (*d*, *J* = 3.2, 1H, H–C(6) or H–C(4)); 3.84 (*sept.*, *J* = 6.7, 1H, H_{anti}–C(N)); 1.52 (*d*, *J* = 6.7, 6H, $(CH_3)_2$C(N) presumably *anti*); 1.34 (*d*, *J* = 6.7, 6H, $(CH_3)_2$C(N) presumably *syn*). – MS.: 219 (11, M^+); 176 (14, $M^+ - C_3H_7$); 135 (10) and 134 (100, $M^+ - C_3H_7 - C_3H_6$).

$C_{13}H_{17}NS$ (219.35) Calc. C 71.18 H 7.81% Found C 71.02 H 8.00%

2-Diisopropylamino-6-(2′-diisopropylaminotropon-7′-yl)-3,7-dehydrotropone (**5**). A yellow solution of 100 mg (0.5 mmol) 2-diisopropylamino-3,7-dehydrotropone (**1**) in 0.5 ml CF_3COOH, which slowly turned deeply red, was allowed to stand for 5 days at 20°, during which time the disappearance of **1** was monitored by TLC. Quenching with sat. $NaHCO_3$-solution followed by extraction with CH_2Cl_2 yielded 100 mg of a reddish oil which was passed through a short alox column, eluting with CH_2Cl_2. The orange-coloured residue obtained by evaporation of the eluate crystallized on standing. Recrystallization from ether gave 25 mg (25%) of **5** as orange-red plates, which sintered slowly upon heating above 130°. – UV. (C_2H_5OH): 234 (20300), 282 (22600), 305 *S* (18000), 403 (11300), 465 (13500). – IR. ($CHCl_3$): 1730*s*, 1635*s*, 1550*m*, 1450*m*. – ^{1}H-NMR. (360 MHz, $CDCl_3$): 8.07 (*d*, *J* = 3.6, 1H, H–C(5)); 7.70 (*d*, *J* = 9.3, 1H, H–C(6′)); 6.68 (*d*×*d*, *J* = 10.2 and 10.2, 1H, H–C(4′)); 6.55 (*d*, *J* = 10.2, 1H, H–C(3′)); 6.48 (*d*, *J* = 3.6, 1H, H–C(4)); 6.47 (*d*×*d*, *J* = 9.3 and 10.2, 1H, H–C(5′)); 5.22 (*sept.*, *J* = 6.6, 1H, H_{syn}–C$(CH_3)_2$–N–C(2))[4]; 4.00 (*sept.*, *J* = 6.6, 3H, H_{anti}–C$(CH_3)_2$–N–C(2) and 2×*H*–C$(CH_3)_2$–N–C(2′)); 1.51 (*d*, *J* = 6.6, 6H, $(CH_3)_2$CH–N–C(2) *anti*); 1.42 (*d*, *J* = 6.6, 6H, $(CH_3)_2$CH–N–C(2) *syn*); 1.34 (*d*, *J* = 6.6, 12H, 2×$(CH_3)_2$CH–N–C(2′)). – On irradiation at 8.07 (H–C(5)) the doublet at 6.48 (H–C(4)) collapsed to a singlet, clarifying the one-proton signal at 6.47 as a *d*×*d*, *J* = 10.2 and 9.3 (H–C(5′)). – On irradiation at 7.70 (H–C(6′)) the signal at 6.47 (H–C(5′)) collapsed to a doublet (*J* = 10.2). Irradiation at the 12-proton signal at 1.34 (*d*, methyl groups of tropone moiety) caused an 18% NOE-enhancement of the signal at 6.55 (*d*, H–C(3′)), while the signal at 7.70 (*d*, H–C(6′)) remained unchanged. – Irradiation at the one-proton septet signal at 5.22 (H_{syn}–C$(CH_3)_2$–N–C(2)) converted the 6-proton doublet at 1.42 ($(CH_3)_2$CH–N–C(2) *syn*) to a singlet. – Irradiation at the 6-proton signal at 1.51 ($(CH_3)_2$CH–N–C(2) *anti*) caused an enhancement of the signal group between 6.49 and 6.45 (which includes the H–C(4) doublet at 6.48 and the central line of the H–C(5′) triplet at 6.47) by 14% while the two side lines of the H–C(5′) triplet as well as the three signals at 7.70 (*d*, H–C(6′)), 6.68 (*d*×*d*, H–C(4′)) and at 6.55 (*d*, H–C(3′)) remained unchanged. We conclude that the NOE-enhancement is on H–C(4) and that it amounts to an estimated 18%. – MS.: 406 (80, M^+), 363 (67), 336 (46), 321 (100), 279 (78).

$C_{26}H_{34}N_2O_2$ (406.57) Calc. C 76.81 H 8.43 N 6.89% Found C 76.54 H 8.66 N 6.69%

4-Deuterio-2-diisopropylamino-6-(3′,4′,6′-trideuterio-2′-diisopropylaminotropon-7′-yl)-3,7-dehydrotropone ([$^2H_4$]-**5**). A similar experiment to the preceding one using CF_3COOD gave [$^2H_4$]-**5**, m.p. sintering above 140°. – ^{1}H-NMR. (100 MHz, $CDCl_3$): 8.07 (*s*, H–C(5)); 6.47 (*s*, H–C(5′)); 5.22 (*sept.*, *J* = 7, 1 H, H_{syn}–C(CH_3)$_2$–N–C(2)); 4.00 (*sept.*, 3 H, H_{anti}–C(CH_3)$_2$–N–C(2) and 2 × *H*–C(CH_3)$_2$–N–C(2′)); 1.51 (*d*, *J* = 7, 6 H, (C*H*$_3$)$_2$CH–N–C(2) *anti*); 1.42 (*d*, *J* = 7, 6 H, (C*H*$_3$)$_2$CH–N–C(2) *syn*); 1.34 (*d*, *J* = 7, 12 H, 2 × (CH_3)$_2$CH–N–C(2′)). When this spectrum of ($^2H_4$]-**5** is compared with that of **5**, one sees that H–C(4), H–C(3′), H–C(4′) and H–C(6′) of **5** have been replaced by ^{2}H-atoms in [$^2H_4$]-**5**. – The mass spectrum showed $M^+ = 410$, which corresponds to an incorporation of four ^{2}H-atoms.

Other spectral measurements. In order to enable direct comparison, the following spectral data of 2-diisopropylamino-3,7-dehydrotropone (**1**) and of 2-dimethylaminotropone (**3**), the latter prepared according to [7], were recorded:

Data of **1**. – ^{1}H-NMR. (60 MHz, CCl_4): 7.32 (*d* × *d*, *J* = 3.6 and 3.2, 1 H, H–C(5)); 6.25 (*d*, *J* = 3.6, 1 H, H–C(4)); 6.20 (*d*, *J* = 3.2, 1 H, H–C(6)); 5.03 (*sept.*, *J* = 6.5, 1 H, H_{syn}–C(CH_3)$_2$); 3.84 (*sept.*, *J* = 6.5, 1 H, H_{anti}–C(CH_3)$_2$); 1.55 (*d*, *J* = 6.5, 6 H, (CH_3)$_2$CH presumably *anti*); 1.40 (*d*, *J* = 6.5, 6 H, (CH_3)$_2$C presumably *syn*). These signals are identical with respect to the coupling pattern and very similar with respect to chemical shift to those reported at 100 MHz [1] for a $CDCl_3$-solution of **1**.

Data of **3**. – IR. ($CHCl_3$): 1615*m*, 1580 *S*, 1556*s*. – ^{1}H-NMR. (360 MHz, $CDCl_3$): 7.00 (*d* × *d* × *d*, *J* = 11.5, 8.0 and 1.0, 1 H, H–C(6)); 6.95 (*d* × *d* × *d*, *J* = 10.1, 10.1 and 1.0, 1 H, H–C(4)); 6.86 (*d*, *J* = 11.5, 1 H, H–C(7)); 6.49 (*d* × *d*, *J* = 10.1 and 8.0, 1 H, H–C(5)); 6.43 (*d*, *J* = 10.1, 1 H, H–C(3)); 3.02 (*s*, 6 H, (CH_3)$_2$N). – Irradiation at the 6-proton signal at 3.02 (*s*, methyl groups) showed a 10% NOE-enhancement of the signal at 6.43 (*d*, H–C(3)), while all the signals in the range between 7.1 and 6.7 (which includes H–C(7)) remained unchanged.

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