

98. The Crystal structure of 2-Diisopropylamino-3,7-dehydrotropone¹⁾

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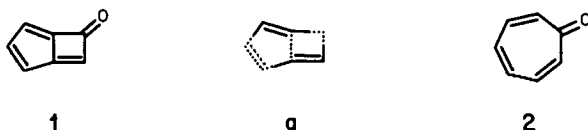
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Zusammenfassung

Die erste Röntgenstrukturanalyse eines 3,7-Dehydrotropone (1)-Derivates, nämlich von 2-Diisopropylamino-3,7-dehydrotropone (4) zeigt das Ringsystem in 4 als planaren Bicyclus mit nahezu C_{2v} -Symmetrie. Dementsprechend enthalten Dehydrotropone formell zwei *trans*-konfigurierte Doppelbindungen in einem 7-gliedrigen Ring; auch das O-Atom und das N-Atom mit seinen Ligandatomen liegen in derselben Ebene wie die Ringatome. Die Bindung zwischen den beiden C-Atomen, welche die Heteroatome tragen, (C(1) and C(2)), ist wesentlich länger (1,56 Å) als die anderen Bindungen im Ringsystem (1,37–1,46 Å). Dies impliziert eine 'push-pull'- π -Elektronen-Delokalisierung, in der auch das O- und das N-Atom involviert sind, und macht eine 'aromatische' Ring-Delokalisierung weniger wahrscheinlich. Im Gegensatz zu 2-(*t*-Butyl)-3,7-dehydrotropone (3) existiert das 2-Diisopropylamino-3,7-dehydrotropone (4) im Kristall als Monomeres, was dem stabilisierenden Einfluss der 'push-pull'-Delokalisierung zugeschrieben werden kann.

1. Introduction. – The derivatives of 3,7-Dehydrotropone (1)³⁾ are of interest because of the subtle interplay between stabilizing and destabilizing factors [1]. On the destabilizing side is the angle strain, which becomes evident when 1 is viewed as possessing two *trans* double bonds in a seven-membered ring (see a),



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

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³⁾ The systematic name for 1 is bicyclo[3.2.0]-1(7),2,4-heptatrien-6-one.

a feature which is not present in the derivatives of tropone (**2**). On the stabilizing side one might consider the cyclic $(4n+2)$ - π -electron delocalization (see **b**) or, in the case of the 2-dialkylamino-3,7-dehydrotropone, the linear push-pull π -electron delocalization (see **c**). Both delocalization effects should support the coplanarity of the atoms involved and cause some equalization of the order of certain bonds. These features are found in some derivatives of **2**.



In this connection, it is of interest that 2-(*t*-butyl)-3,7-dehydrotropone (**3**)⁴ has been found to crystallize as a [4+2]-dimer, which dissociates when dissolved, and that the monomer **3** in solution redimerizes thermally in a [6+4]-fashion with subsequent loss of carbon monoxide [2]. 2-Diisopropylamino-3,7-dehydrotropone (**4**)⁵, on the other hand, is thermally stable but dimerizes in trifluoroacetic acid solution with cleavage of the C(3), C(7)-bond [3].



To confirm the unusual ring system of 3,7-dehydrotropone derivatives, the structure of which had previously been deduced only from spectroscopic data, and to ascertain whether **4** crystallizes as a monomer or - as in the case of **3** - as a dimer, we undertook an X-ray structure determination of **4**. We were also interested in the structural parameters of a 3,7-dehydrotropone system for theoretical reasons (see also footnote 8 in [3]).

2. X-Ray structure analysis of 2-diisopropylamino-3,7-dehydrotropone (4). - Crystals grown from an acetone solution of **4** were suitable for an X-ray single crystal structure analysis. The space group is monoclinic, $P2_1/b$, with $a = 13.68$ (1), $b = 14.51$ (1), $c = 6.687$ (4) Å, $\gamma = 114.3$ (1)° and with four molecules per unit cell. A syntax diffractometer was used for the measurement of 775 reflections of which 631 with $I > 3\sigma(I)$ were considered observed. The program system XRAY [4] was used for phase determination and structure refinement. H-Atoms could be picked out from a difference *Fourier* map and were refined isotropically. The refinement converged to $R = 0.049$ ($R_w = 0.048$). The final coordinates are given in the *Table*.

⁴) The systematic name for **3** is 7-(*t*-butyl)bicyclo[3.2.0]-1(7),2,4-heptatrien-6-one.

⁵) The systematic name for **4** is 7-diisopropylaminobicyclo[3.2.0]-1(7),2,4-heptatrien-6-one. Note that our numbering of C-atoms in **4** does not correspond to the systematic name.

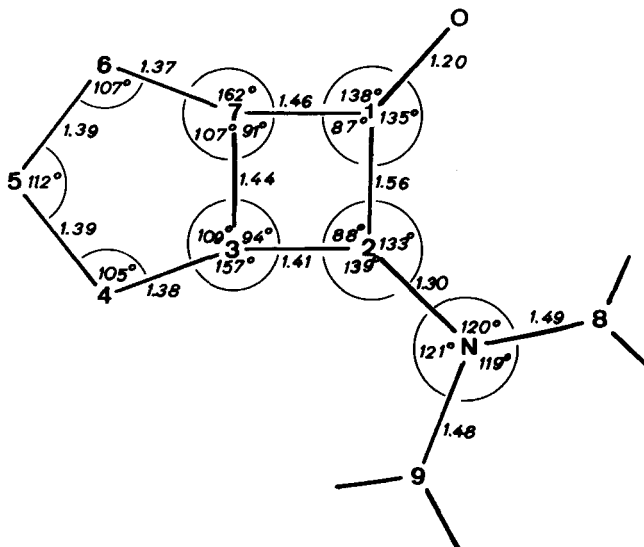


Fig. 1. Selected bond lengths and angles of 2-diisopropylamino-3,7-dehydrotropone (4) (The upper limits of the estimated standard deviations are 0.01 Å for the distances and 1° for the angles)

No uncommon values for the anisotropic temperature factors were observed. Selected bond distances and angles are given in *Figure 1* and a stereoscopic drawing of the molecule is shown in *Figure 2*.

The standard deviation of the atoms from the least-squares plane of the ring atoms C(1) through C(7), the heteroatoms O and N, and C(8) and C(9), bonded to N, is only 0.016 Å, which means that the 3,7-dehydrotropone ring system, including its ligand atoms, is very nearly planar.

3. Discussion. – The results of the X-ray analysis confirm the structure of the 3,7-dehydrotropone ring system in 4, with C(3) and C(7) in bonding distance (1.44 Å) and all ring C-atoms trigonal and planar in a five- and a four-membered

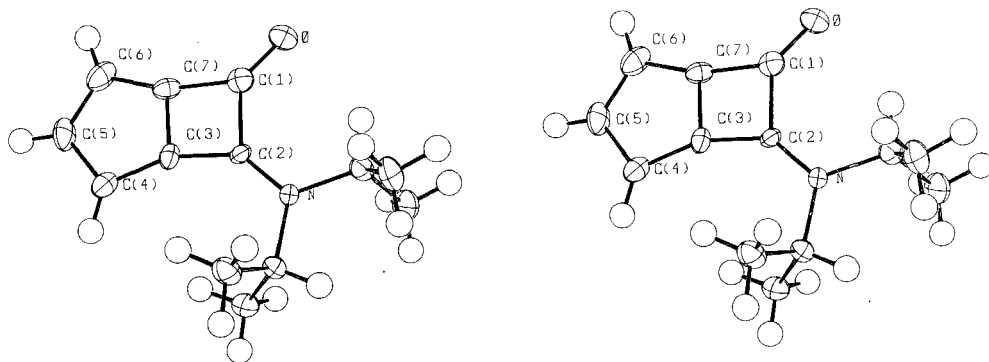


Fig. 2. Stereoscopic drawings of 2-diisopropylamino-3,7-dehydrotropone (4) (ORTEP II, [5])

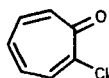
Table. *Positional parameters of the atoms of 2-diisopropylamino-3,7-dehydrotropone (4) in fractions of cell edges* (The standard deviations, given in parentheses, refer to the last significant digit)

Atom	X	Y	Z
N	0.2054 (4)	-0.0290 (4)	0.2253 (8)
O	0.1202 (4)	0.1442 (3)	0.3522 (8)
C (1)	0.1962 (7)	0.1284 (5)	0.402 (1)
C (2)	0.2398 (6)	0.0483 (5)	0.345 (1)
C (3)	0.3247 (7)	0.0955 (6)	0.480 (1)
C (4)	0.4166 (7)	0.1093 (6)	0.586 (1)
H (4)	0.455 (4)	0.068 (4)	0.589 (9)
C (5)	0.4355 (7)	0.1928 (7)	0.708 (1)
H (5)	0.490 (5)	0.216 (4)	0.794 (9)
C (6)	0.3586 (8)	0.2314 (6)	0.679 (1)
H (6)	0.353 (5)	0.284 (4)	0.736 (9)
C (7)	0.2883 (7)	0.1717 (6)	0.537 (1)
C (8)	0.1075 (5)	-0.0512 (5)	0.103 (1)
H (8)	0.084 (4)	0.003 (4)	0.129 (8)
C (9)	0.2627 (5)	-0.0957 (5)	0.206 (1)
H (9)	0.221 (4)	-0.145 (4)	0.111 (8)
C (10)	0.1340 (7)	-0.0480 (7)	-0.116 (1)
H (101)	0.192 (4)	0.017 (4)	-0.155 (9)
H (102)	0.150 (4)	-0.105 (4)	-0.155 (9)
H (103)	0.076 (4)	-0.049 (4)	-0.203 (9)
C (11)	0.0178 (6)	-0.1492 (6)	0.165 (1)
H (111)	-0.046 (4)	-0.155 (4)	0.095 (9)
H (112)	0.034 (4)	-0.203 (4)	0.138 (9)
H (113)	-0.001 (4)	-0.149 (4)	0.309 (9)
C (12)	0.3731 (6)	-0.0378 (6)	0.115 (1)
H (121)	0.407 (4)	-0.088 (4)	0.091 (8)
H (122)	0.421 (4)	0.019 (4)	0.203 (8)
H (123)	0.371 (5)	-0.010 (4)	-0.004 (9)
C (13)	0.2673 (7)	-0.1440 (6)	0.402 (1)
H (131)	0.195 (4)	-0.177 (4)	0.455 (9)
H (132)	0.312 (4)	-0.095 (4)	0.501 (9)
H (133)	0.297 (4)	-0.190 (4)	0.389 (9)

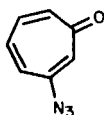
ring, thereby exhibiting two formally *trans*-configured double bonds in the seven-membered ring.

Since the ring C-atoms (C(1) to C(7)), the two heteroatoms (O and N) and the two C-atoms attached to the N-atom (C(8) and C(9)) form an essentially coplanar arrangement there must be considerable π -electron delocalization involving the extra electron pair of N-atom. The fact that the C, C-bonds and C, C, C-bond-angles are equalized in such a way that a C_2 -axis passing through C(5) is closely approximated by the ring system (just a slight deviation is seen in the four-membered ring) shows that the π -electron delocalization involves the entire system and that the two heteroatoms exert only a slightly different influence. These effects of the π -electron delocalization in **4** are similar to – and even somewhat more pronounced than – those in tropone (**2**) [6], 2-chlorotropone (**5**) [7], 3-azidotropone (**6**) [8] and tropolone (**7**) [9].

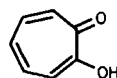
The C(1), C(2)-bond in **4** is particularly long, of the order of a single bond (1.56 Å). This suggests a push-pull π -electron delocalization involving the two heteroatoms and only a weak contribution (if at all) of the cyclic $(4n+2)$ - π -electron delocalization. A similar, but smaller, lengthening of the corresponding bond occurs in **5** (1.48 Å) [7] and **7** (1.45 Å) [9].



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The X-ray results show that **4** crystallizes as the monomer. Evidently, the 2-dialkylamino-group (in **4**) is able to stabilize the 3,7-dehydrotropone system more effectively than a 2-(*t*-butyl)-group (in **3**) [2]. This lends support to the postulated importance of the push-pull delocalization in **4**.

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