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### 5-Acetyl-7-(*N*-methylanilino)cyclohepta-2,4-dien-1-one, C<sub>16</sub>H<sub>17</sub>NO<sub>2</sub>

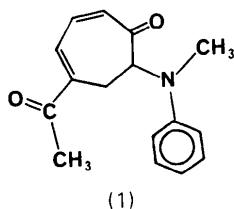
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**Abstract.**  $M_r = 255.32$ , orthorhombic,  $P2_12_12_1$ ,  $a = 6.219$  (2),  $b = 14.176$  (5),  $c = 15.432$  (4) Å,  $V = 1360.5$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.25$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu = 0.76$  cm<sup>-1</sup>,  $F(000) = 544$ ,  $T = 298$  K,  $R = 0.099$  for 1133 unique observed reflections. An interesting feature of this molecule is the very close intramolecular nonbonded N...O distance of 2.69 (1) Å; this appears to result in displacements of some atoms from what would otherwise be coplanar configurations. The methylanilino group is in the pseudo-equatorial position, with its plane nearly perpendicular (87°) to the best plane of the diene-dione system.

**Introduction.** 5-Acetyl-7-(*N*-methylanilino)cyclohepta-2,4-dien-1-one (1) is an intermediate in the course of synthesis of 4-vinyltropone from 2-(1-acetoxyethyl)tropone. The red color and UV spectrum of (1) have been interpreted as resulting from some form of electron donor–acceptor complexation (Bugner, 1982).



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**Experimental.** Preparation according to a modification (Bugner, 1982) of a synthesis developed by Dennis, Katritzky, Parton, Nomura, Takahashi & Takeuchi (1976) and adapted by Jackson (1980); red, blade-shaped, single crystal, 0.14 × 0.14 × 0.40 mm; Weissenberg photographs have systematic absences  $h00$  for  $h$  odd,  $0k0$  for  $k$  odd,  $00l$  for  $l$  odd; Syntex  $P\bar{1}$  diffractometer, graphite monochromator, unit-cell parameters by least-squares refinement of 15 reflections ( $16.45 \leq 2\theta \leq 22.23^\circ$ ),  $\theta$ – $2\theta$  scan,  $4.0^\circ \text{ min}^{-1}$  in  $2\theta$ ,  $2\theta_{\text{max}} = 50^\circ$  for range  $0 \leq h \leq 7$ ,  $0 \leq k \leq 16$ ,  $0 \leq l \leq 18$ , three reflections monitored every 97 reflections with 2% maximum intensity variation from average, average variation  $\pm 1\%$ , e.s.d. of standards about 1%, 1317 unique data, 1133 with  $I > 0$  used in subsequent calculations, Lorentz and polarization but no absorption correction; direct methods, all atoms (including H atoms) located on Fourier and difference Fourier maps. The phenyl ring was treated as a rigid C<sub>6</sub>H<sub>5</sub> group, C–C = 1.395 Å, C–H 1.0 Å, C–C–C and C–C–H = 120°, with individual isotropic displacement parameters for C and fixed isotropic displacement parameters for each H atom based on that of the attached C. All other H atoms were kept in geometrically reasonable positions with C–H = 1.0 Å and with fixed displacement parameters, as described for those attached to phenyl C atoms. All other nonhydrogen atoms have anisotropic displacement parameters; refined by full-matrix least-squares procedure based on  $F$  with

maximum  $\sin\theta/\lambda = 0.59 \text{ \AA}^{-1}$ ; refinement of 130 parameters converged to  $R = 0.099$ ,  $wR = 0.077$ ,  $w = 1/\sigma^2(F_o)$ , error of fit = 1.57, ratio in final cycle of maximum least-squares shift to e.s.d. 0.064 in a displacement parameter and 0.045 in a positional parameter; maximum and minimum heights of 0.1 and  $-0.1 \text{ e \AA}^{-3}$  in final difference Fourier synthesis; atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974); all calculations performed on DEC VAX 11/750 and VAX 11/780 computers using the *UCLA Crystallographic Package* (1984) (locally edited versions of *CARESS*, *PROFILE*, *MULTAN*, *ORFLS*, *ORFFE*, *ABSORB*, *ORTEP*, *PLUTO*, *SHELX*, and a local molecular-geometry program, *MG84*).

**Discussion.** Atomic coordinates and isotropic displacement parameters are listed in Table 1; bond lengths and angles and torsion angles are given in Table 2.\* There is no significant delocalization evident from the bond distances in the diene-dione system that extends from O(1) to O(8). A *PLUTO* stereoview of the molecule is shown in Fig. 1. The short O(1)⋯N contact [2.69 (1) Å] is evident in the stereoview; such close intramolecular interactions of a carbonyl O atom and a N atom separated from the carbonyl group by one intervening C atom occur whenever the corresponding O—C—C—N torsion angle is not far from 0°, e.g. when it is constrained by a ring system. In the present molecule the O—C—C—N torsion angle is  $-16^\circ$ . We have been unable to find other examples of such a close contact in a diene-dione system, but a search of the Cambridge Database (Allen, Bellard, Brice, Cartwright, Doubleday, Higgs, Hummelink, Hummelink-Peters, Kennard, Motherwell, Rodgers & Watson, 1979) revealed a number of similar contacts in other systems, some involving trigonal N atoms with their plane of hybridization more or less normal to the O⋯N line, as in the present molecule. They are all characterized by O⋯N distances around 2.6 to 2.7 Å. The methylanilino group is in the pseudo-equatorial position, with its plane nearly perpendicular ( $87^\circ$ ) to the best plane of the diene-dione system. The N atom is displaced 0.07 Å from the least-squares plane through the methylanilino group, in a direction away from O(1); the methyl C atom is displaced 0.19 Å to the opposite side of this plane. Presumably these displacements are a consequence of a repulsive interaction between O(1) and N(12), which are about 0.2 Å closer than the sum of their van der Waals radii. The O⋯N line makes an

Table 1. Atomic coordinates and displacement parameters for 5-acetyl-7-(*N*-methylanilino)cyclohepta-2,4-dien-1-one

O(1)	$\langle u^2 \rangle_{\text{eq}} = [1/(8\pi^2)]B_{\text{eq}}$ (as defined by Hamilton, 1959).			$\langle u^2 \rangle_{\text{eq}}/\langle u^2 \rangle$ (Å <sup>2</sup> )
	<i>x</i>	<i>y</i>	<i>z</i>	
O(1)	0.6479 (9)	0.2951 (3)	0.8055 (3)	0.082 (12)
C(2)	0.6481 (12)	0.3705 (5)	0.7688 (5)	0.054 (2)
C(3)	0.5215 (11)	0.4486 (5)	0.8051 (4)	0.059 (2)
C(4)	0.4752 (12)	0.5315 (5)	0.7680 (5)	0.062 (3)
C(5)	0.5446 (12)	0.5730 (4)	0.6875 (5)	0.055 (2)
C(6)	0.7326 (12)	0.5549 (4)	0.6482 (4)	0.050 (2)
C(7)	0.8001 (15)	0.6077 (5)	0.5695 (5)	0.064 (3)
O(8)	0.9787 (11)	0.5979 (4)	0.5408 (4)	0.103 (3)
C(9)	0.6462 (17)	0.6742 (5)	0.5263 (5)	0.086 (4)
C(10)	0.8841 (11)	0.4818 (3)	0.6804 (4)	0.048 (2)
C(11)	0.7795 (10)	0.3829 (4)	0.6856 (4)	0.046 (2)
N(12)	0.9341 (9)	0.3075 (3)	0.6752 (3)	0.050 (2)
C(13)	1.1086 (14)	0.3054 (5)	0.7369 (6)	0.087 (3)
C(14)	0.8932 (6)	0.2268 (2)	0.6259 (3)	0.038 (2)
C(15)	0.7048 (6)	0.2175 (2)	0.5776 (3)	0.046 (2)
C(16)	0.6732 (6)	0.1380 (2)	0.5259 (3)	0.057 (2)
C(17)	0.8300 (6)	0.0677 (2)	0.5225 (3)	0.055 (2)
C(18)	1.0185 (6)	0.0770 (2)	0.5708 (3)	0.060 (2)
C(19)	1.0501 (6)	0.1566 (2)	0.6225 (3)	0.054 (2)

Table 2. Bond distances (Å), bond angles (°) and torsion angles (°) for 5-acetyl-7-(*N*-methylanilino)cyclohepta-2,4-dien-1-one

E.s.d. in parentheses in units of least-significant digit of the corresponding value.

O(1)—C(2)	1.209 (8)	C(2)—C(3)	1.470 (10)
C(2)—C(11)	1.533 (10)	C(3)—C(4)	1.339 (10)
C(4)—C(5)	1.441 (10)	C(5)—C(6)	1.342 (10)
C(6)—C(7)	1.486 (10)	C(6)—C(10)	1.487 (9)
C(7)—O(8)	1.203 (11)	C(7)—C(9)	1.500 (12)
C(10)—C(11)	1.547 (8)	C(11)—N(12)	1.447 (8)
N(12)—C(13)	1.443 (10)	N(12)—C(14)	1.398 (6)
O(1)—C(2)—C(3)	119.2 (6)	O(1)—C(2)—C(11)	119.6 (6)
C(3)—C(2)—C(11)	121.2 (6)	C(2)—C(3)—C(4)	127.9 (6)
C(3)—C(4)—C(5)	131.5 (7)	C(4)—C(5)—C(6)	124.9 (6)
C(5)—C(6)—C(7)	121.3 (6)	C(5)—C(6)—C(10)	122.3 (6)
C(7)—C(6)—C(10)	116.4 (6)	C(6)—C(7)—O(8)	120.2 (7)
C(6)—C(7)—C(9)	119.9 (7)	O(8)—C(7)—C(9)	119.8 (7)
C(6)—C(10)—C(11)	112.5 (5)	C(2)—C(11)—C(10)	111.8 (5)
C(2)—C(11)—N(12)	111.3 (5)	C(10)—C(11)—N(12)	112.6 (5)
C(11)—N(12)—C(13)	116.3 (5)	C(11)—N(12)—C(14)	123.0 (5)
C(13)—N(12)—C(14)	118.6 (5)	N(12)—C(14)—C(15)	121.4 (4)
N(12)—C(14)—C(19)	118.5 (4)		
O(1)—C(2)—C(3)—C(4)	-169.0 (7)	O(1)—C(2)—C(11)—C(10)	-142.7 (6)
O(1)—C(2)—C(11)—N(12)	-15.8 (9)	C(3)—C(2)—C(11)—C(10)	37.4 (8)
C(3)—C(2)—C(11)—N(12)	164.3 (6)	C(11)—C(2)—C(3)—C(4)	10.9 (11)
C(2)—C(3)—C(4)—C(5)	-5.6 (13)	C(3)—C(4)—C(5)—C(6)	-28.1 (13)
C(4)—C(5)—C(6)—C(7)	-174.1 (7)	C(4)—C(5)—C(6)—C(10)	5.8 (11)
C(5)—C(6)—C(7)—O(8)	171.8 (8)	C(5)—C(6)—C(7)—C(9)	-7.5 (11)
C(5)—C(6)—C(10)—C(11)	57.4 (8)	C(7)—C(6)—C(10)—C(11)	-122.7 (7)
C(10)—C(6)—C(7)—O(8)	-8.2 (10)	C(10)—C(6)—C(7)—C(9)	172.6 (7)
C(6)—C(10)—C(11)—C(2)	-82.0 (7)	C(6)—C(10)—C(11)—N(12)	151.9 (6)
C(2)—C(11)—N(12)—C(13)	-67.9 (7)	C(2)—C(11)—N(12)—C(14)	95.0 (6)
C(10)—C(11)—N(12)—C(13)	58.5 (7)	C(10)—C(11)—N(12)—C(14)	-138.6 (5)
C(11)—N(12)—C(14)—C(15)	5.2 (7)	C(11)—N(12)—C(14)—C(19)	-177.7 (5)
C(13)—N(12)—C(14)—C(15)	167.7 (6)	C(13)—N(12)—C(14)—C(19)	-15.2 (7)

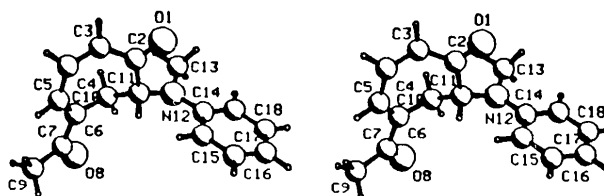


Fig. 1. Stereoview of the molecule, showing the numbering scheme.

\* Lists of structure factors, anisotropic displacement parameters and hydrogen-atom parameters and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42206 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

angle of  $24^\circ$  with the normal to the plane. The hybridization at the N atom is not far from  $sp^2$ , with an unshared electron pair in a  $p$  orbital directed toward one of the  $sp^2$  orbitals on O(1), which is occupied by an unshared pair on that atom. Study of molecular models suggests that the methylanilino group could comfortably occupy a pseudo-axial position, which would place the phenyl ring above the diene-dione system. Apparently, however, that conformation is not favored even in solution; NMR evidence (Bugner, 1982) indicates that the conformation found in the crystal (Fig. 1) is also present in  $CDCl_3$  solution.

There are no unusual intermolecular distances; the shortest intermolecular distance not involving hydrogen is  $3.35 \text{ \AA}$ , from O(8) to C(17)( $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$ ).

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## $(C_6H_3OCH_3)_6(CH_2)_2S$ , An Expanded Hemispherand

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**Abstract.** 34,35,36,37,38,39-Hexamethoxy-28-thiaheptacyclo[28.3.1.1<sup>2,6</sup>.1<sup>7,11</sup>.1<sup>12,16</sup>.1<sup>17,21</sup>.1<sup>22,26</sup>]nonatriaconta-1-(34),2,4,6(39),7,9,11(38),12,14,16(37),17,19,21(36),22,24,26(35),30,32-octadecaene,  $C_{44}H_{40}O_6S$ ,  $M_r = 696.87$ , monoclinic,  $Cc$ ,  $a = 12.693(4)$ ,  $b = 18.382(9)$ ,  $c = 16.009(7) \text{ \AA}$ ,  $\beta = 99.50(3)^\circ$ ,  $V = 3684(3) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_x = 1.26 \text{ g cm}^{-3}$ ,  $\lambda(\text{Mo } K\alpha) = 0.7107 \text{ \AA}$ ,  $\mu = 1.26 \text{ cm}^{-1}$ ,  $F(000) = 1472$ ,  $T = 295 \text{ K}$ ,  $R = 0.092$  for 3155 unique nonzero reflections. The molecule has an approximate (non-crystallographic) twofold axis. The methoxy methyl groups nearest to the  $-\text{CH}_2-\text{S}-\text{CH}_2-$  unit turn inward, occupying the cavity of this uncomplexed host molecule. The remaining four methoxy methyl groups are directed outward, in an alternating up-down-up-down arrangement. The  $-\text{CH}_2-\text{S}-\text{CH}_2-$  linkage provides conformational flexibility relative to the prototype spherand,  $(\text{CH}_3\text{OC}_6\text{H}_2\text{CH}_3)_6$ .

**Introduction.** Hemispherands have been defined as hosts for which at least half of the cavity has been preorganized during synthesis, but which must undergo partial conformational reorganization during complexation (Cram & Trueblood, 1981). The title compound (1) was designed, with the help of CPK molecular models, to have a cavity complementary to larger monatomic cations, such as  $\text{K}^+$  and  $\text{Rb}^+$ , and in fact does complex these two cations more strongly than it does either  $\text{Na}^+$  or  $\text{Cs}^+$  (Cram, deGrandpre, Knobler & Trueblood, 1984).

**Experimental.** (1) prepared as described (Cram *et al.*, 1984) and recrystallized from  $\text{CH}_2\text{Cl}_2/\text{benzene}$ . Colorless parallelepiped,  $0.35 \times 0.36 \times 0.50 \text{ mm}$ , Syntex  $P\bar{1}$  diffractometer, graphite monochromator, orientation matrix and unit-cell dimensions from 15 carefully centered reflections with  $2\theta < 24^\circ$ ; intensities measured for  $2\theta < 50^\circ$  ( $h_{\text{max}} = 15$ ,  $k_{\text{max}} = 20$ ,  $l = -18$  to 18),  $\theta$ - $2\theta$  scan,  $4^\circ \text{ min}^{-1}$  in  $2\theta$ , from  $1^\circ$  below  $K\alpha_1$  to  $1^\circ$  above  $K\alpha_2$ ; intensities of three standard reflections

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