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Structure of *N,O*-Dibenzoyl-*N-o*-tolylhydroxylamine,* $C_{21}H_{17}NO_3$

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Abstract. $M_r = 331{\cdot}4$, triclinic, $P\bar{1}$, $a = 11{\cdot}268\,(4)$, $b = 9{\cdot}970\,(3)$, $c = 8{\cdot}801\,(2)$ Å, $\alpha = 104{\cdot}30\,(6)$, $\beta = 87{\cdot}71\,(2)$, $\gamma = 113{\cdot}25\,(2)°$, $V = 864{\cdot}3$ Å^3, $Z = 2$, $D_x = 1{\cdot}27$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7109$ Å, $\mu = 0{\cdot}49$ cm^{-1}, $F(000) = 314$, $T = 294\,(2)$ K, $R = 0{\cdot}052$ for 2793 reflections with $I > 3\sigma(I)$. The conformation of the molecule in the crystal is the minor one of the three observed in liquid-media ^{1}H NMR spectroscopy. The benzene ring of the anilide is *exo* (*trans* to the oxygen atom). There are no hydrogen bonds and no short intermolecular distances.

Introduction. Most carcinogenic compounds are active because they are metabolized to a highly reactive electrophilic intermediate which reacts with macromolecular cellular constituents to initiate the carcinogenic event (Lhoëst, Razzouk & Mercier, 1976).

N-hydroxylation of primary amines is an example of an unusual metabolic reaction where the product is more reactive, and in some cases more toxic than the parent compounds. The *N*-hydroxy derivative is considered as being the approximate carcinogenic product. Esterification of an *N*-hydroxylated function is necessary to observe *in vitro* reaction with nucleophilic components.

For these reasons, we have endeavoured to develop a complete study of the *N,O*-dibenzoyl-*N-o*-tolylhydroxylamine (1), a compound obtained from *o*-nitrotoluene and benzoyl chloride with one equivalent of lithium diisopropylamidate (Couturier, Roussel & Ricard, 1983; Roussel, 1982).

The conformations have been studied by low-temperature ^{1}H NMR. Electrophilic nitrenium species in equilibrium with the carbenium structure are detected by chemical ionization desorption mass spectrometry.

The present paper is devoted to an X-ray crystallographic structure determination of (1) to show that one of the three conformations observed in the liquid has been retained in the solid state.

Fig. 1 displays the results obtained from ^{1}H NMR analysis, where an equilibrium is achieved between the different conformations.

Experimental. Single crystal $0{\cdot}3 \times 0{\cdot}5 \times 0{\cdot}4$ mm, Philips PW 1100 four-circle diffractometer, lattice parameters from 25 reflections ($20 < \theta < 27°$); data collection: ω–2θ scan, width of scan fixed to 1·2°; 4183 intensities with $\sin\theta/\lambda \leq 0{\cdot}703$ Å^{-1}, $-15 \leq h \leq 15$, $-13 \leq k \leq 13$, $0 \leq l \leq 11$, 3 standard reflections monitored at intervals of 2 h (3% variation); 2793 reflections with $I > 3\sigma(I)$; Lp correction, absorption and extinction ignored; *MULTAN* (Germain, Main & Woolfson, 1971) and Fourier methods, anisotropic full matrix on F (Sheldrick, 1976), H from $\Delta\rho$ synthesis, isotropic, not refined; final $R_w = 0{\cdot}052$, unit weights, $S = 3{\cdot}82$; $\Delta\rho$ in final map $= 0{\cdot}5$, $-0{\cdot}4$ e Å^{-3}, $(\Delta/\sigma)_{\max} = 0{\cdot}15$; atomic scattering factors from *International Tables for X-ray Crystallography* (1974), for H from Stewart, Davidson & Simpson (1965).

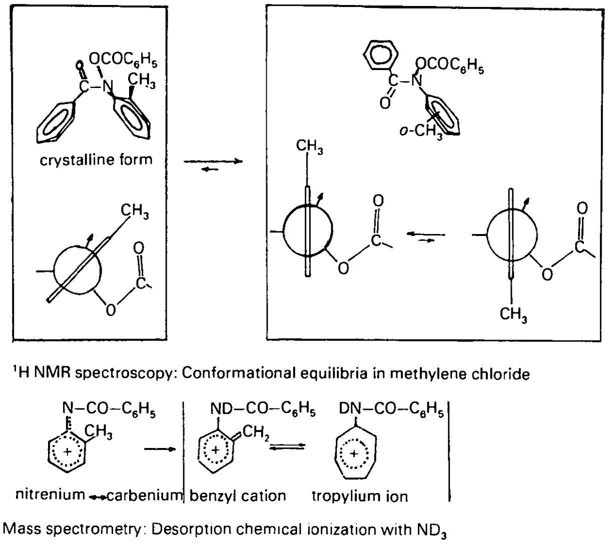

Fig. 1. Results obtained from ^{1}H NMR analysis.

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* *N*-Benzoyloxy-*N*-(*o*-tolyl)benzamide.

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Table 1. *Atomic positional parameters* ($\times 10^4$) *and equivalent isotropic temperature factors* (Å^2 $\times 10^2$) *with e.s.d.'s in parentheses*

$$U_{\rm eq}=\tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
N	7413 (2)	−244 (2)	1304 (2)	49 (2)
O(1)	7862 (2)	673 (2)	2825 (2)	57 (2)
C(1)	7590 (2)	1984 (2)	3213 (2)	65 (3)
O(2)	7047 (2)	2323 (2)	2371 (2)	91 (3)
C(2)	8112 (2)	2868 (2)	4789 (3)	56 (2)
C(3)	8544 (2)	2272 (2)	5788 (3)	59 (3)
C(4)	9055 (3)	3159 (3)	7220 (3)	67 (3)
C(5)	9149 (3)	4654 (3)	7650 (3)	63 (3)
C(6)	8701 (3)	5247 (3)	6691 (4)	83 (4)
C(7)	8183 (3)	4368 (3)	5265 (3)	82 (3)
C(8)	8259 (2)	296 (2)	120 (3)	51 (2)
O(3)	9213 (2)	1467 (2)	384 (2)	51 (2)
C(9)	7847 (2)	−603 (2)	−1492 (3)	46 (2)
C(10)	8797 (2)	−720 (3)	−2600 (3)	56 (3)
C(11)	8458 (3)	−1490 (3)	−4123 (3)	76 (3)
C(12)	7186 (3)	−2119 (3)	−4546 (3)	63 (4)
C(13)	6240 (3)	−1989 (3)	−3474 (4)	64 (4)
C(14)	6560 (3)	−1239 (3)	−1936 (3)	62 (3)
C(15)	6882 (2)	−1839 (3)	1382 (3)	44 (2)
C(16)	7680 (2)	−2669 (3)	1019 (3)	55 (3)
C(17)	7207 (3)	−4160 (3)	1164 (3)	74 (4)
C(18)	5955 (3)	−4813 (3)	1673 (4)	62 (4)
C(19)	5184 (3)	−4013 (3)	2022 (4)	60 (3)
C(20)	5622 (2)	−2487 (3)	1890 (3)	66 (3)
C(21)	4769 (3)	−1631 (4)	2241 (5)	127 (5)

Table 2. *Bond lengths* (Å) *and bond angles* (°), *with e.s.d.'s in parentheses*

N–O(1)	1·432 (3)	C(9)–C(10)	1·387 (4)
N–C(8)	1·390 (3)	C(9)–C(14)	1·391 (4)
N–C(15)	1·451 (3)	C(10)–C(11)	1·377 (4)
O(1)–C(1)	1·388 (3)	C(11)–C(12)	1·372 (5)
C(1)–O(2)	1·190 (4)	C(12)–C(13)	1·368 (5)
C(1)–C(2)	1·484 (4)	C(13)–C(14)	1·381 (4)
C(2)–C(3)	1·386 (4)	C(15)–C(16)	1·399 (4)
C(2)–C(7)	1·396 (4)	C(15)–C(20)	1·381 (4)
C(3)–C(4)	1·378 (4)	C(16)–C(17)	1·377 (4)
C(4)–C(5)	1·382 (4)	C(17)–C(18)	1·374 (5)
C(5)–C(6)	1·368 (4)	C(18)–C(19)	1·351 (5)
C(6)–C(7)	1·374 (4)	C(19)–C(20)	1·407 (4)
C(8)–O(3)	1·215 (3)	C(20)–C(21)	1·470 (5)
C(8)–C(9)	1·487 (3)		

N–C(8)–O(3)	122·3 (2)	C(15)–C(20)–C(19)	116·9 (3)
N–C(8)–C(9)	114·6 (2)	C(15)–C(20)–C(21)	121·5 (3)
O(3)–C(8)–C(9)	122·9 (2)	C(19)–C(20)–C(21)	121·6 (3)
C(8)–C(9)–C(10)	118·0 (2)	O(1)–N–C(8)	111·9 (2)
C(8)–C(9)–C(14)	122·2 (2)	O(1)–N–C(15)	108·9 (2)
C(10)–C(9)–C(14)	119·7 (2)	C(8)–N–C(15)	122·8 (2)
C(9)–C(10)–C(11)	119·8 (2)	N–O(1)–C(1)	113·2 (2)
C(10)–C(11)–C(12)	120·0 (3)	O(1)–C(1)–O(2)	123·8 (2)
C(11)–C(12)–C(13)	120·8 (3)	O(1)–C(1)–C(2)	109·1 (2)
C(12)–C(13)–C(14)	119·9 (3)	O(2)–C(1)–C(2)	127·1 (2)
C(9)–C(14)–C(13)	119·7 (3)	C(1)–C(2)–C(3)	122·7 (2)
N–C(15)–C(16)	119·2 (2)	C(1)–C(2)–C(7)	118·2 (2)
N–C(15)–C(20)	119·5 (2)	C(3)–C(2)–C(7)	119·1 (2)
C(16)–C(15)–C(20)	121·2 (2)	C(2)–C(3)–C(4)	120·3 (2)
C(15)–C(16)–C(17)	119·7 (2)	C(3)–C(4)–C(5)	119·6 (3)
C(16)–C(17)–C(18)	119·5 (3)	C(4)–C(5)–C(6)	120·7 (3)
C(17)–C(18)–C(19)	120·8 (3)	C(5)–C(6)–C(6)	120·0 (3)
C(18)–C(19)–C(20)	121·9 (3)	C(2)–C(7)–C(6)	120·2 (3)

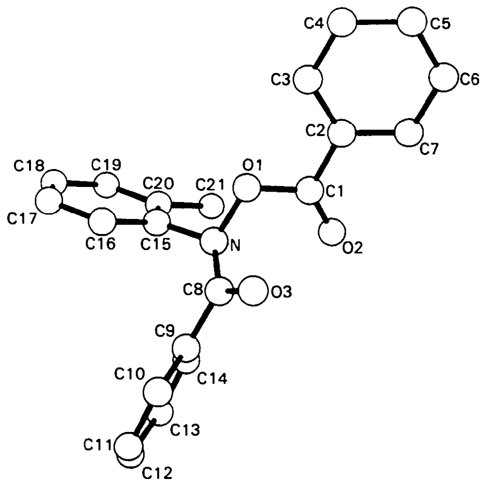

Fig. 2. Perspective view of the molecule.

Discussion. Table 1 gives atomic coordinates, Table 2 bond lengths and angles and Fig. 2 a view of the molecule with atom numbering.[*]

The conformation of the molecule in the crystal is one of the three observed in the liquid media by NMR spectroscopy; the benzene ring of the anilide is *exo* (*trans* to the oxygen atom).

There is no hydrogen bonding, and no intermolecular distances between the molecules are less than the sum of the van der Waals radii, except one between C(19) and C(18) which is 3·385 (10) Å.

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[*] Lists of structure factors, anisotropic thermal parameters, hydrogen-atom parameters, least-squares planes and Newman projections have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39246 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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