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The Crystal and Molecular Structure of 3-[1-(Phenylamino)ethylidene]-6-methyl-2,4-dioxo-2,3-dihydro-4*H*-pyran

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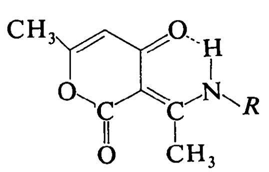
The crystal and molecular structure of 3-[1-(phenylamino)ethylidene]-6-methyl-2,4-dioxo-2,3-dihydro-4*H*-pyran has been determined by single-crystal X-ray techniques. Crystals are monoclinic, space group $P2_1/a$, with a = 12·895 (8), b = 7·913 (5), c = 11·867 (6) Å, β = 91·2 (1)° and Z = 4. The structure was solved by direct methods and refined by least-squares calculations to a conventional R of 0·066 for 1209 reflexions with $I > 2\sigma(I)$ measured on a diffractometer. Both the phenyl and pyran rings are planar within experimental error and make an angle of 47·3° with each other. A single intramolecular N—H···O=C(5) hydrogen bond is present.

Introduction

β-Amino-enediones having both carbonyls embodied in a pyrrolidine, pyrrole, furan or pyridine heterocycle exist at room temperature as diastereomeric pairs, in different relative ratios, due to the pertinent intramolecular hydrogen bonds. In contrast, ^{1}H-NMR spectra of the related 3-[α-(amino)ethylidene]-2,4-dioxo-2,3-dihydro-4*H*-pyrans clearly indicated the presence of a single species. Structures bearing the NH chelated only to the enone carbonyl were accordingly assigned to the latter products [(1), R = H or CH_3, Caramella & Querci (1971); R = $CHCH_3COOC_2H_5$, iso-C_3H_7 or C_6H_5, Filira, Acampora, Giormani, Rothstein & D'Angeli (1978)].



(1)

Whereas no crystals suitable for X-ray analysis were hitherto obtained from solutions of the compounds existing as diastereomeric pairs, such crystals were easily obtained in the case of the pyran derivative (1*a*) ($R = C_6H_5$).

A detailed crystallographic study of the title compound (1*a*) has been carried out. We present here its crystal and molecular structure, while still endeavouring to obtain specimens representative of the series mentioned above.

Experimental

Transparent needle-shaped crystals of 3-[1-(phenylamino)ethylidene]-6-methyl-2,4-dioxo-2,3-dihydro-4*H*-pyran elongated along a, were obtained by slow evaporation from a solution in ethanol.

Lattice constants were obtained from a least-squares analysis of the setting angles of reflexions measured on a four-circle diffractometer with Mo $K\bar{\alpha}$ radiation monochromatized by a graphite crystal. The intensities were collected from a crystal of approximate dimensions 0·40 × 0·35 × 0·24 mm, on a Philips PW 1100 four-circle diffractometer operating in the $\theta/2\theta$ scan mode (scan width = 1·5°, scan speed = 0·03° s^{-1}). 2126 independent reflexions up to θ = 25° were measured, of which 1209 had $I > 2\sigma(I)$, σ being calculated from the counting statistics of the measurements. During the data collection two standard reflexions were measured every 120 min to check the stability of the crystal and electronics. Intensities were corrected for Lorentz and polarization factors and were converted to the absolute scale by Wilson's method. Absorption and extinction corrections were not applied.

Structure determination and refinement

The positions of the non-hydrogen atoms were determined by direct methods. Normalized structure factors were calculated and the 250 reflexions with $|E(hkl)| > 1{\cdot}8$ were used in the phasing program *MULTAN* (Germain, Main & Woolfson, 1971). An *E* map was calculated and the structural solution was evident. The conventional *R* value was 0·23. The structure was refined by full-matrix least-squares methods with anisotropic thermal parameters giving an *R* of 0·085. At this point difference Fourier maps were calculated in order to locate the hydrogen atoms. All the hydrogen atom positions were easily located and included in the refinement with isotropic thermal parameters equivalent to the anisotropic ones of the atoms to which the hydrogens are bonded (Hamilton, 1959). The final refinements were done in two sections: (*a*) the parameters involving the hydrogen atoms ($R = 0{\cdot}075$) and (*b*) all non-hydrogen atom parameters. The final *R* value for the 1209 reflexions with $I > 2\sigma(I)$ was 0·066. The refinement was carried out minimizing the quantity $\sum w(|F_o| - |F_c|)^2$, $w = 1{\cdot}1[1 + (|F_o| - 8)/12]^2$, to give constant values of $w\Delta^2$ ($\Delta = |F_o| - |F_c|$), independent of the value of $|F_o|$.

The calculations were carried out on the CYBER 76 computer of the 'Centro di Calcolo Inter-universitario Italia Nord Orientale' with the XRAY system of crystallographic programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). All atomic scattering factors were those of *International Tables for X-ray Crystallography* (1974).

Results and discussion

A perspective view of the molecule showing its conformation and the numbering system is presented in Fig. 1. Crystal data are given in Table 1. The final structural parameters, with their e.s.d.'s of the non-hydrogen and H atoms are reported in Tables 2 and 3 respectively; in Table 4 the bond lengths and valence angles for all non-hydrogen atoms, not corrected for changes due to thermal vibrations, are given.* The

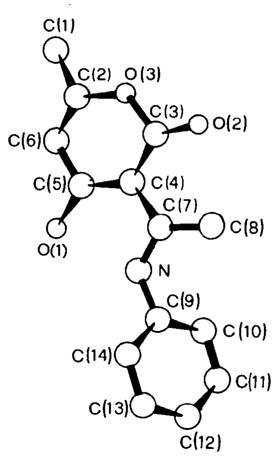


Fig. 1. Perspective view of the molecule with the numbering system.

Table 1. *Crystal data*

$C_{14}H_{13}NO_3$	$M_r = 243{\cdot}26$
Space group $P2_1/a$	$Z = 4$
λ(Mo $K\bar{\alpha}$) = 0·7107 Å	$V = 1210{\cdot}6$ Å^3
a = 12·895 (8) Å	$D_o = 1{\cdot}33$ g cm^{-3}
b = 7·913 (5)	$D_c = 1{\cdot}33$
c = 11·867 (6)	$F(000) = 128$
β = 91·2 (1)°	μ(Mo $K\bar{\alpha}$) = 1·02 cm^{-1}

Table 2. *Final positional parameters and their standard deviations for non-hydrogen atoms*

	x	*y*	*z*
O(1)	0·0463 (2)	0·8235 (5)	0·6062 (3)
O(2)	0·3332 (3)	0·9542 (6)	0·8473 (3)
O(3)	0·1841 (3)	0·8754 (5)	0·9142 (3)
N	0·2138 (3)	0·9066 (6)	0·5152 (3)
C(1)	0·0390 (5)	0·7687 (8)	1·0106 (5)
C(2)	0·0857 (4)	0·8152 (7)	0·9016 (4)
C(3)	0·2454 (4)	0·9152 (7)	0·8221 (4)
C(4)	0·1978 (3)	0·8996 (6)	0·7109 (4)
C(5)	0·0937 (4)	0·8416 (6)	0·7002 (4)
C(6)	0·0399 (3)	0·7987 (7)	0·8010 (4)
C(7)	0·2579 (3)	0·9368 (6)	0·6148 (4)
C(8)	0·3641 (3)	1·0110 (7)	0·6203 (4)
C(9)	0·2567 (3)	0·9146 (6)	0·4052 (4)
C(10)	0·3500 (4)	0·8396 (7)	0·3806 (4)
C(11)	0·3816 (4)	0·8390 (8)	0·2694 (5)
C(12)	0·3211 (5)	0·9083 (9)	0·1859 (5)
C(13)	0·2289 (5)	0·9830 (8)	0·2110 (5)
C(14)	0·1947 (4)	0·9855 (7)	0·3210 (4)

Table 3. *Fractional coordinates for the hydrogen atoms, with e.s.d.'s in parentheses*

	x	*y*	*z*
H'(C1)	0·026 (4)	0·880 (7)	1·053 (4)
H''(C1)	−0·020 (4)	0·665 (7)	0·990 (4)
H'''(C1)	0·076 (4)	0·694 (6)	1·050 (4)
H(C6)	−0·041 (4)	0·780 (7)	0·798 (4)
H'(C8)	0·416 (4)	0·923 (7)	0·632 (4)
H''(C8)	0·394 (4)	1·072 (7)	0·544 (4)
H'''(C8)	0·386 (4)	1·100 (7)	0·693 (4)
H(C10)	0·398 (4)	0·784 (6)	0·435 (4)
H(C11)	0·449 (4)	0·787 (7)	0·253 (4)
H(C12)	0·346 (4)	0·908 (7)	0·103 (4)
H(C13)	0·181 (4)	1·031 (7)	0·150 (4)
H(C14)	0·128 (4)	1·028 (7)	0·342 (4)
H(N)	0·140 (4)	0·914 (6)	0·512 (4)

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33540 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Intramolecular bond distances and angles with e.s.d.'s in parentheses*

O(1)–C(5)	1·269 (6)	O(3)–C(3)–C(4)	117·2 (4)
O(2)–C(3)	1·205 (6)	C(10)–C(9)–C(14)	121·0 (4)
O(3)–C(2)	1·361 (6)	C(1)–C(2)–O(3)	112·6 (4)
O(3)–C(3)	1·398 (6)	C(1)–C(2)–C(6)	125·4 (5)
N–C(7)	1·323 (6)	C(2)–O(3)–C(3)	122·3 (4)
N–C(9)	1·423 (6)	O(3)–C(3)–O(2)	114·0 (4)
C(1)–C(2)	1·484 (8)	O(2)–C(3)–C(4)	128·7 (5)
C(3)–C(4)	1·449 (7)	C(3)–C(4)–C(5)	119·3 (4)
C(4)–C(5)	1·421 (7)	C(3)–C(4)–C(7)	119·0 (4)
C(4)–C(7)	1·423 (7)	C(4)–C(5)–O(1)	123·5 (4)
C(5)–C(6)	1·436 (7)	O(1)–C(5)–C(6)	118·2 (4)
C(2)–C(6)	1·326 (7)	C(4)–C(5)–C(6)	118·3 (4)
C(7)–C(8)	1·490 (7)	C(5)–C(6)–C(2)	120·8 (5)
C(9)–C(10)	1·379 (7)	C(6)–C(2)–O(3)	122·0 (4)
C(10)–C(11)	1·390 (8)	C(5)–C(4)–C(7)	121·6 (4)
C(11)–C(12)	1·364 (9)	C(4)–C(7)–C(8)	124·2 (4)
C(12)–C(13)	1·366 (9)	C(4)–C(7)–N	116·6 (4)
C(13)–C(14)	1·386 (8)	C(8)–C(7)–N	119·2 (4)
C(9)–C(14)	1·385 (7)	C(7)–N–C(9)	129·8 (4)
		N–C(9)–C(10)	122·0 (4)
		C(9)–C(10)–C(11)	118·5 (5)
		C(10)–C(11)–C(12)	120·9 (6)
		C(11)–C(12)–C(13)	120·2 (6)
		C(12)–C(13)–C(14)	120·5 (6)
		C(13)–C(14)–C(9)	118·9 (5)
		N–C(9)–C(14)	116·6 (4)

Table 5. *Deviations* (Å) *of the atoms from some least-squares planes in the molecule, with their dihedral angles*

The equations of the planes are in the form $AX + BY + CZ = D$ in orthogonal ångström space with X parallel to a, Z perpendicular to a in the plane of a and c and Y perpendicular to the plane of a and c. An asterisk denotes the atoms not used in the plane calculation.

Plane (1): $-0{\cdot}3359X + 0{\cdot}9404Y + 0{\cdot}0519Z = 6{\cdot}3361$

C(6)	−0·005	C(4)	−0·001
C(2)	−0·010	C(3)	−0·014
C(5)	0·010	O(3)	0·020
C(1)*	−0·078	O(1)*	0·016
C(7)*	−0·052	O(2)*	−0·086
C(8)*	0·044	N*	−0·16
		H(N)	−0·22

Plane (2): $0{\cdot}4593X + 0{\cdot}8767Y + 0{\cdot}1428Z = 8{\cdot}5024$

C(9)	0·003	C(12)	−0·006
C(10)	−0·003	C(13)	0·006
C(11)	0·004	C(14)	−0·005
N*	−0·13	H(N)*	−0·52

Plane (3): $-0{\cdot}3121X + 0{\cdot}9500Y + 0{\cdot}0004Z = 6{\cdot}0142$

N	−0·027	C(5)	−0·024
O(1)	0·025	C(7)	0·029
C(4)	−0·004	H(N)*	0·33

Dihedral angles (°) between planes

1–2	47·3
1–3	3·3
2–3	46·4

Table 6. *Torsion angles* (°)

The torsion angle of the bonded group A–X–Y–B is the angle between the planes A–X–Y and X–Y–B. It is positive if clockwise and negative if counterclockwise (Klyne & Prelog, 1960).

C(4)–C(7)–N–C(9)	173·1
C(7)–N–C(9)–C(10)	48·3

C—H lengths of the phenyl ring are in the range 0·98–1·01 Å, while the remaining ones range from 0·90 to 1·14 Å. Some least-squares planes and torsion angles are shown in Tables 5 and 6 respectively.

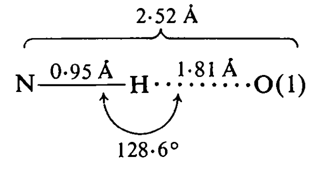
Bond lengths and valence angles of the phenyl ring, which is planar within experimental error, range from 1·364–1·390 Å and 118·5–121·4° respectively; the mean of the bond lengths, 1·378 Å, is shorter than the accepted value of 1·397 Å, the shortening being probably due to libration effects, as the thermal motion of the atoms of the benzene ring is large; in contrast, the mean of the angles, 120°, represents the standard value. The disposition of bonds about nitrogen is approximately planar; the N—C(9) distance of 1·423 Å is longer than is frequently observed, but compares well with 1·43 Å in acetanilide (Brown & Corbridge, 1954). In addition, this bond is bent about 5° with respect to the phenyl plane, which is also tilted by 47·3° from the plane in which the rest of the molecule lies. Conjugation between the nitrogen and the benzene ring seems therefore greatly reduced.

The values of the N—C(7), C(7)—C(4), C(4)—C(5) and C(5)—O(1) distances, along with the planarity of this part of the molecule, strongly indicate that resonance extends from N to O(1) through C(7), C(4) and C(5).

As for the remaining part of the molecule we note that the pyran ring is planar within experimental error with valence angles close to 120°; this would suggest the presence of a conjugated system, although some bond distances are significantly different from the standard values (Pauling, 1960). In particular, both C(2)—C(6) and C(3)—O(2) are very close the double-bond value, while the double-bond character for C(5)—C(6) and C(3)—C(4) is less than 25%. This value increases to about 35% for C(4)—C(5), which nevertheless is involved in the conjugated system from N to O(1).

The C(1)—C(2) and C(7)—C(8) distances of 1·484 and 1·490 Å are slightly short for a Csp^2—Csp^3 distance.

An important feature of the molecule is the intramolecular N—H···O(1) hydrogen bond which is characterized by:



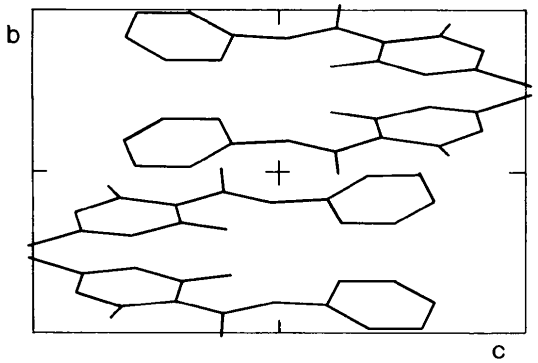


Fig. 2. The crystal structure projected down *a*.

The N···O distance is significantly shorter than frequently observed values (Donohue, 1968) and can be justified only by the molecular geometry. As regards other relevant intramolecular contact distances, the values for C(8)···O(2) (2·77 Å) and C(8)···C(10) (3·16 Å) are less than the van der Waals distances.

The packing of the planar pyran and phenyl rings is shown in Fig. 2. All intermolecular distances correspond to standard van der Waals contacts.

We thank Professor F. D'Angeli for helpful discussions and suggestions during this work.

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Etude Structurale de l'Oxyde *trans* d'α,β-Dicyano-stilbène

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Dicyanostilbene oxide crystallizes in the monoclinic system, space group $P2_1/c$, with parameters $a = 9{\cdot}337$ (5), $b = 11{\cdot}196$ (3), $c = 12{\cdot}067$ (3) Å and $\beta = 90{\cdot}52$ (4)°. There are four molecules in the unit cell. The structure was determined by direct methods and refined by least-squares methods to $R = 0{\cdot}052$. The compound exhibits a *trans* configuration. Such structural results permit a satisfactory explanation of the spiropentaoxyphosphorane thermal decomposition in terms of an inversion of the configuration.

Introduction

Mukaiyama, Kuwajima & Ohno (1965) ont étudié la thermolyse de l'éthoxyphosphorane (1). La réduction par la tributylphosphine de l'époxyde (2) obtenu, conduit au *cis* dicyanostilbène (3). Cette réduction s'effectuant avec inversion de configuration, les auteurs attribuent la structure *trans* à l'époxyde (2) et la