

for 1394 observed [$I > 2\sigma(I)$] reflections and 331 refined parameters. All the structural parameters quoted in Table 2 and discussed in the *Comment* are from the F^2 refinement. The atomic coordinates of Table 1 correspond to the absolute structure assumed on the basis of the Flack (1983) index, $x = 0.04$ (3). Comparison of the results of the two refinements by means of half-normal probability plots (Abrahams & Keve, 1971) gave the following regression parameters:

	i	s	r	N	$(\Delta/\sigma)_{\max}$
d	0.019 (6)	0.680 (6)	0.996	125	1.92
U_{ij}	0.016 (5)	0.704 (5)	0.996	138	2.13
xyz	-0.119 (14)	0.909 (14)	0.992	69	2.47

where d represents all interatomic distances < 4.65 Å, U_{ij} the atomic displacement parameters, xyz the positional coordinates and i is the intercept, s the slope, r the correlation coefficient and N the number of points in the plot defining the regression line. The values of i and s indicate that there are no relevant systematic errors and that the e.s.d.'s are overestimated by a factor of 1.4 for the d 's and U_{ij} 's and by a factor of 1.1 for the coordinates.

Calculations were performed using the ENCORE91 and GOULD-POWERNODE 6040 computers of the Centro di Studio per la Strutturistica Diffraattometrica del CNR (Parma).

Cell refinement: *LQPARM* (Nardelli & Mangia, 1984). Program used to solve the structure: *SHELXS86* (Sheldrick, 1985). Programs used to refine the structure: *SHELX76* (Sheldrick, 1976) and *SHELXL93* (Sheldrick, 1994). Molecular graphics: *ORTEP* (Johnson, 1965). Software used for geometric calculations: *PARST* (Nardelli, 1983b). Software used to prepare material for publication: *PARSTCIF* (Nardelli, 1991).

Financial support from the European Community Commission under contract No. SC1000657 is gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: LI1099). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1,2-Dihydro-8-methyl-4(3*H*)-carbazolone Prepared by a New Arynic Cyclization Reaction

SANDRA IANELLI, MARIO NARDELLI* AND
DANIELE BELLETTI

*Dipartimento di Chimica Generale ed Inorganica,
Chimica Analitica, Chimica Fisica,
Università degli Studi di Parma,
Centro di Studio per la Strutturistica Diffraattometrica
del CNR, Viale delle Scienze 78, I-43100 Parma, Italy*

CATERINE CAUBÈRE, PAUL CAUBÈRE AND
BRIGITTE JAMART-GRÉGOIRE

*Laboratoire de Chimie Organique I,
UA CNRS No. 457, Université de Nancy I,
BP 239, 54506 Vandoeuvre-Les-Nancy CEDEX, France*

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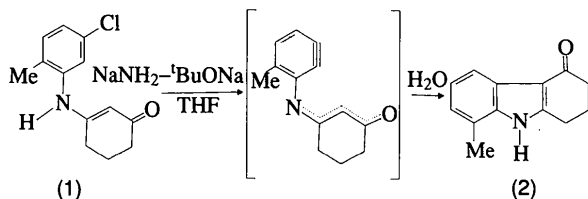
Abstract

Of the two possible keto–enol tautomeric species of the title compound, $C_{13}H_{13}NO$, it is the keto one that is found in the crystal; it involves an intermolecular N—H···O=C hydrogen bond between molecules, related

by the $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$ symmetry operation of the $P2_1/n$ space group, which run in chains along the x axis. IR data of the solid product are assigned and it is deduced from the ^1H and ^{13}C NMR spectra that this hydrogen bond is also active in solution in DMSO. The relevant structural parameters of the molecule in the crystal are compared with those calculated by molecular mechanics for the isolated structure.

Comment

During the synthesis of indoles by aryne condensation of unsubstituted enaminketones in the presence of the NaNH_2 - $t\text{BuONa}$ complex base (Caubère, Caubère, Renard, Bizot-Espiart & Jamart-Grégoire, 1993) according to the scheme below, we had to define the structure of the product (2) obtained. The spectral data of (2) were intriguing: the IR spectrum of the solid product indicated two absorption bands (at 3170 and 1610 cm^{-1}) and ^1H NMR studies in DMSO/ CDCl_3 solution showed a proton exchangeable with D_2O at 11.5 p.p.m. These characteristics seemed to support an enol structure. However, these data agreed with those for similar compounds (Masaguer, Ravina & Fueyo, 1992) which had been assigned the keto form. Crystal structure analysis of (2) was performed in order to establish unequivocally the form of the molecule in this crystal.



As shown by the *ORTEP* (Johnson, 1965) drawing (Fig. 1) and the data in Table 2, the keto tautomer is present in the crystal in which the molecules are joined in chains along the x axis by the following hydrogen bond in which the N atom acts as donor to the keto O atom: $\text{N1}\cdots\text{H1N} = 0.95(3)$, $\text{N1}\cdots\text{O1}^i = 2.787(4)$, $\text{H1N}\cdots\text{O}^i = 1.87(3)$ Å, $\text{N1}\cdots\text{H1N}\cdots\text{O1}^i = 162(3)^\circ$; symmetry code: (i) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$. Two conclusions may be drawn from this: (a) the 3170 and 1610 cm^{-1} IR absorption bands must be assigned to the strongly associated NH and $\text{C}=\text{O}$ groups, respectively, and (b) such interactions must continue to be active in solution. The *N*-methanesulfonate derivative of (2) was prepared and its IR spectrum obtained. This showed the expected conjugated $\text{C}=\text{O}$ absorption at 1650 cm^{-1} and there were no HO characteristics in the NMR spectrum, all of which supports conclusion (b).

In Table 2, the values of bond distances and angles found in the crystal are compared with those calculated for the isolated molecules of the two tautomeric species by *PCMODEL-MMX* (Serena Software, 1989) and *HYPERCHEM-MM+* (Autodesk, 1992) start-

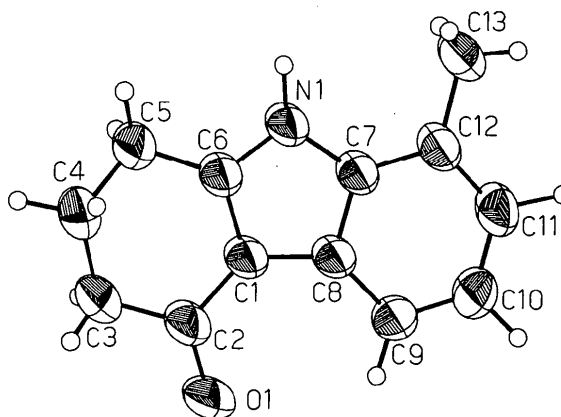


Fig. 1. *ORTEP* (Johnson, 1965) drawings of the molecule. Displacement ellipsoids are drawn at the 50% probability level.

ing from the experimental coordinates and using the default input parameters. The purpose of these calculations was to show that, although the accuracy of the crystal structure analysis is not high, the results are nevertheless quite reliable, particularly with regard to the conclusion that the molecule is the keto tautomer. In this respect, it is also important to note that the geometry of the observed hydrogen bond agrees quite satisfactorily with the average geometry found for this bond from neutron diffraction [$\text{H}\cdots\text{O} = 1.865(16)$, $\text{N}\cdots\text{O} = 2.849(12)$ Å, $\text{N}\cdots\text{H}\cdots\text{O} = 161.5(15)^\circ$ (Taylor & Kennard, 1983)].

It is interesting to observe that only one of the two possible states [(I) and (II)] of the hydrogen-bonded chain is observed; the fact that the intermediate one in which the disordered proton occupies two positions (one near to N and the other near to O) corresponding to two energy wells is not seen is indicative that the $\text{N}\cdots\text{H}\cdots\text{O}=\text{C}$ hydrogen-bond system is energetically favoured.



Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$)

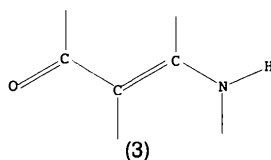
$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
N1	0.3825 (2)	0.1382 (2)	0.1005 (3)	0.0740 (9)
O1	0.0753 (2)	0.3105 (2)	−0.1900 (3)	0.1004 (11)
C1	0.2332 (2)	0.2279 (3)	−0.0386 (3)	0.0685 (9)
C2	0.1668 (3)	0.3310 (3)	−0.1274 (4)	0.0760 (11)
C3	0.2136 (3)	0.4655 (4)	−0.1442 (6)	0.0957 (16)
C4	0.3139 (3)	0.4930 (4)	−0.0205 (6)	0.0994 (17)
C5	0.3886 (3)	0.3795 (3)	0.0082 (6)	0.0906 (14)
C6	0.3363 (2)	0.2512 (3)	0.0247 (3)	0.0704 (10)
C7	0.3103 (2)	0.0380 (2)	0.0910 (3)	0.0667 (11)
C8	0.2151 (2)	0.0912 (3)	0.0033 (3)	0.0654 (11)
C9	0.1292 (3)	0.0084 (3)	−0.0248 (4)	0.0755 (11)
C10	0.1426 (3)	−0.1227 (3)	0.0316 (4)	0.0833 (14)
C11	0.2374 (3)	−0.1737 (3)	0.1169 (4)	0.0798 (12)
C12	0.3240 (3)	−0.0953 (3)	0.1479 (4)	0.0730 (11)
C13	0.4269 (3)	−0.1491 (4)	0.2372 (6)	0.0924 (16)

Table 2. Comparison of bond distances (Å) and bond angles (°)

	X-ray data	PCMODEL-MMX		HYPERCHEM-MM+		CSD mean
		keto	enol	keto	enol	
N1—C6	1.352 (3)	1.360	1.275	1.344	1.351	1.352 (3)
N1—C7	1.389 (4)	1.366	1.274	1.342	1.348	—
O1—C2	1.239 (4)	1.211	1.353	1.211	1.359	1.238 (5)
C1—C2	1.430 (4)	1.474	1.340	1.355	1.342	1.452 (5)
C1—C6	1.389 (4)	1.336	1.343	1.342	1.344	1.397 (8)
C1—C8	1.434 (4)	1.343	1.341	1.340	1.339	—
C2—C3	1.501 (5)	1.528	1.510	1.526	1.513	—
C3—C4	1.499 (6)	1.540	1.536	1.536	1.535	—
C4—C5	1.497 (5)	1.537	1.535	1.533	1.533	—
C5—C6	1.483 (5)	1.494	1.499	1.496	1.502	—
C7—C8	1.414 (4)	1.346	1.342	1.395	1.392	—
C7—C12	1.396 (4)	1.341	1.342	1.394	1.396	—
C8—C9	1.403 (4)	1.339	1.339	1.393	1.393	—
C9—C10	1.374 (4)	1.344	1.344	1.399	1.398	—
C10—C11	1.396 (5)	1.345	1.345	1.400	1.399	—
C11—C12	1.385 (5)	1.346	1.347	1.401	1.400	—
C12—C13	1.503 (5)	1.507	1.508	1.506	1.507	—
C6—N1—C7	108.9 (2)	105.7	109.5	107.3	101.5	—
C6—C1—C8	106.9 (3)	108.0	105.5	109.4	106.0	—
C2—C1—C8	131.8 (3)	130.5	131.2	127.6	131.5	—
C2—C1—C6	121.2 (3)	121.5	123.3	123.1	122.6	121.9 (11)
O1—C2—C1	122.1 (3)	125.3	123.5	123.8	124.9	123.5 (6)
C1—C2—C3	116.7 (3)	113.8	119.4	116.9	119.9	—
O1—C2—C3	121.3 (3)	120.8	117.1	119.3	115.1	—
C2—C3—C4	116.1 (3)	114.1	111.9	113.5	111.7	—
C3—C4—C5	115.8 (4)	111.7	111.5	110.3	110.1	—
C4—C5—C6	109.4 (3)	106.7	108.8	107.7	109.0	—
C1—C6—C5	125.3 (3)	128.3	124.0	125.8	123.6	—
N1—C6—C5	124.8 (2)	122.2	126.5	125.3	122.0	—
N1—C6—C1	109.9 (3)	109.5	109.6	109.0	114.5	—
N1—C7—C12	128.8 (2)	128.7	128.9	128.1	125.1	—
N1—C7—C8	108.1 (3)	108.8	109.0	108.7	112.1	—
C8—C7—C12	123.1 (2)	122.6	122.1	123.2	122.8	—
C1—C8—C7	106.1 (2)	108.0	106.5	105.7	105.9	—
C7—C8—C9	119.2 (3)	120.1	120.8	120.1	120.1	—
C1—C8—C9	134.8 (3)	131.9	132.7	134.2	134.0	—
C8—C9—C10	117.8 (3)	118.3	117.9	117.8	118.2	—
C9—C10—C11	122.2 (3)	121.1	121.0	121.3	121.1	—
C10—C11—C12	121.9 (3)	121.3	121.4	121.4	121.2	—
C7—C12—C11	115.9 (3)	116.7	116.8	116.1	116.7	—
C11—C12—C13	122.6 (3)	122.3	122.2	122.5	122.1	—
C7—C12—C13	121.5 (3)	121.0	121.1	121.4	121.3	—

In order to obtain further confirmation of the observed keto structure, a search of the 1993 release of the Cambridge Structural Database (CSD; Allen *et al.*, 1991) for fragment (3) was performed; 35 entries were found which satisfied the conditions $R < 0.07$ and $\sigma(\text{C—C}) \leq 0.01$ Å. The relevant averaged parameters, quoted in Table 2 under the CSD heading, agree quite satisfactorily with the results of the present analysis. No entries were found for the corresponding enol fragment. It is worth noting that further searches of the CSD revealed no examples of the $\text{CO—H}\cdots\text{N}$ hydrogen bond.



Analysis of the 'thermal' motion, carried out in terms of the TLS rigid-body approximation (Schomaker & Trueblood, 1968) using the program *THMV* (Trueblood,

1984), gives a fairly good value of the overall residual disagreement index ($R_{wU} = 0.066$) indicating that, in spite of the poor quality of the intensity data, the anisotropic displacement parameters are in agreement with an overall concerted motion of the molecule. The R_{wU} index improves to 0.045 if the internal motions are considered according to Dunitz & White (1973).

Experimental

Crystal data

$\text{C}_{13}\text{H}_{13}\text{NO}$
 $M_r = 199.25$
 Monoclinic
 $P2_1/n$
 $a = 13.706$ (6) Å
 $b = 9.908$ (4) Å
 $c = 8.126$ (3) Å
 $\beta = 105.29$ (3)°
 $V = 1064.4$ (8) Å³
 $Z = 4$
 $D_x = 1.243$ Mg m^{−3}

Cu $K\alpha$ radiation
 $\lambda = 1.5418$ Å
 Cell parameters from 29 reflections
 $\theta = 25\text{--}45^\circ$
 $\mu = 0.622$ mm^{−1}
 $T = 293$ (2) K
 Small prism
 $0.65 \times 0.36 \times 0.29$ mm
 Yellow

Data collection

Siemens AED diffractometer $\theta_{\max} = 70.49^\circ$
 θ - 2θ scans $h = -1 \rightarrow 16$
 Absorption correction: $k = -12 \rightarrow 12$
 none $l = -9 \rightarrow 9$
 3916 measured reflections 1 standard reflection
 2025 independent reflections monitored every 50
 1317 observed reflections reflections
 $[I > 2\sigma(I)]$ intensity variation: within
 $R_{\text{int}} = 0.0675$ statistical fluctuation

Refinement

Refinement on F^2 $\Delta\rho_{\max} = 0.278 \text{ e } \text{\AA}^{-3}$
 $R[F^2 > 2\sigma(F^2)] = 0.0830$ $\Delta\rho_{\min} = -0.215 \text{ e } \text{\AA}^{-3}$
 $wR(F^2) = 0.2314$ Extinction correction:
 $S = 1.114$ $F_c^* = kF_c[1 + (0.001\chi$
 1988 reflections $\times F_c^2\lambda^3/\sin 2\theta)]^{-1/4}$
 189 parameters Extinction coefficient:
 All H-atom parameters 0.010 (3)
 refined Atomic scattering factors
 $w = 1/[\sigma^2(F_o^2) + (0.1742P)^2$ from *International Tables*
 $+ 0.2112P]$ for *Crystallography* 1992,
 where $P = (F_o^2 + 2F_c^2)/3$ Vol. C, Tables 4.2.6.8 and
 $(\Delta/\sigma)_{\max} = 0.011$ 6.1.1.4)

The integrated intensities were obtained by a modified version (Belletti, Ugozzoli, Cantoni & Pasquinelli, 1979) of the Lehmann & Larsen (1974) peak-profile analysis procedure. All reflections were corrected for Lorentz and polarization effects. The structure was solved by direct methods and refined by anisotropic full-matrix least squares. All the H atoms were found in the final $\Delta\rho$ map and refined isotropically with free displacement parameters in spite of the fact that the intensity data were of poor quality as the crystals were affected by twinning.

The calculations were carried out on the ENCORE91 and GOULD-POWERNODE 6040 computers of the Centro di Studio per la Strutturistica Diffattometrica del CNR (Parma).

Data collection: local programs. Cell refinement: *LQPARM* (Nardelli & Mangia, 1984). Data reduction: local programs. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1986). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1994). Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *PARST* (Nardelli, 1983); *PARSTCIF* (Nardelli, 1991).

Financial support from the European Community Commission under contract No. SC1000657 is gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: LI1111). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(6a α ,6b β ,12b β ,12c α)-6a,6b,12b,12c-Tetrahydrocyclobuta[1,2-c:4,3-c']-di[1]benzothiopyran-6,7-dione†

JÜRGEN KOPF AND HARALD MAELGER

Institut für Anorganische und Angewandte Chemie, Universität Hamburg, Martin-Luther-King-Platz 6, D-20146 Hamburg, Germany

CAROLIN THIEMANN AND PAUL MARGARETHA

Institut für Organische Chemie, Universität Hamburg, Martin-Luther-King-Platz 6, D-20146 Hamburg, Germany

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Abstract

Irradiation (350 nm) of 1-thiocoumarin in solution affords the title compound in 55% yield. This compound crystallizes in the chiral space group *P*6₅ with two

† Dedicated to Professor Dr. Dr. h.c. Hansjörg Sinn on the occasion of his 65th birthday.