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Acta Cryst. (1996). C**52**, 2573–2575

A Reinvestigation of the Quinoidal Effect in *N*-*n*-Propyl-2-oxo-1-naphthylidenemethylamine

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(Received 22 January 1996; accepted 7 May 1996)

Abstract

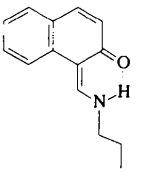
In the title compound $C_{14}H_{15}NO$ (systematic name: 1-*n*-propylaminomethylene-2-naphthalenone), an intramolecular N—H···O hydrogen bond [N···O 2.578 (2), N—H 0.775, H···O 1.936 Å] arises when the hydroxyl-H atom of the Schiff base prepared from 2-hydroxy-1-naphthaldehyde and *n*-propylamine shifts to the N atom. This is the consequence of the pronounced quinoidal effect in the 2-oxo-1-naphthaldimine moiety which has a very short C3=C4 bond of 1.343 (3) Å. The spatial orientation of the *N*-substituent with respect to the rest of the molecule (which is planar) depends on the surroundings of the molecules defined by the crystal packing.

Comment

In a recently published paper on the structure of 2-hydroxy-*N*-*n*-propyl-1-naphthaldimine (Hökelek, Gündüz, Hayvali & Kiliç, 1995), the H atom involved in the intramolecular O—H···N bond was positioned geometrically at 1.0 Å from the donor atom. This proton assignment was obviously inferred from NMR spectroscopy data. This conclusion is in contrast with the results obtained from the study of the dominant tautomeric form of 2-oxo-1-naphthaldimines (Gavranić, Kaitner & Meštrović, 1996).

An investigation of the structures of the ligands themselves was undertaken in order to reveal the presence of either the benzenoid or quinoid form (or the predominant presence of one of them) in the crystalline state. The synthesis and structure of Schiff bases derived from 2-hydroxy-1-naphthaldehyde with various alkyl and aryl *N*-substituents, and their metal complexes have been of interest recently in our laboratory. Bidentate Schiff base ligands derived from aryl aldehydes with a hydroxyl group in position 2 of the aryl ring to which the C=N imino group is bonded have been studied extensively for years. Unfortunately, almost all investigations of the crystal structures of the above-mentioned systems were performed on the aldimine compounds or their metal complexes based on salicylaldehyde (2-hydroxy-1-benzaldehyde). There is a lack of information about similar Schiff base compounds derived from 2-hydroxy-1-naphthaldehyde. The dissimilarity between these two aldehydes arises from the difference in the ring moiety, a single ring compared to a fused double-ring system. The discrepancy appears in the arrangement of the endocyclic bond distances. The characteristic D_{2h} pattern of the naphthalene bond lengths (Allen, Kennard, Watson, Brammer & Orpen, 1987) is preserved in the imino compounds of 2-hydroxy-1-naphthaldehyde and this is the most important feature distinguishing the naphthaldimines from the salicylaldimines. The existence of the enol (or predominantly enol) tautomer has been established in all crystal structures of *N*-substituted salicylaldimines listed so far in the Cambridge Structural Database (October 1995 release). In contrast, no structural data on the tautomeric form assumed in the naphthaldimine derivatives could be found. The predominance of the keto-imine form of 2-hydroxy-1-naphthaldimines in solution was confirmed by NMR spectroscopy (Costamagna, Vargas, Latorre, Alvarado & Mena, 1992).

Our crystallographic studies showed an intramolecular N—H···O hydrogen bond to be present in naphthaldimines in the solid state (Pavlović, Doležal, Gabud & Kaitner, 1995; Gavranić, Kaitner & Meštrović, 1996) regardless of the kind of *N*-substituent, aryl or alkyl. We established the presence in the title compound (I) of an N—H···O hydrogen bond with very similar parameters to those reported by Hökelek *et al.* (1995). In (I), the O···N 'bite' distance is 2.578 (2) Å with N—H1N and O···H1N distances of 0.775 and 1.936 Å, respectively. A view of the title compound is presented in Fig. 1. For clarity, the same atomic numbering scheme as used by Hökelek *et al.* (1995) was adopted. The atom H1N was located from a difference Fourier map as a well defined small electron density maximum of 0.53 e Å^{-3} (Fig. 2).



(I)

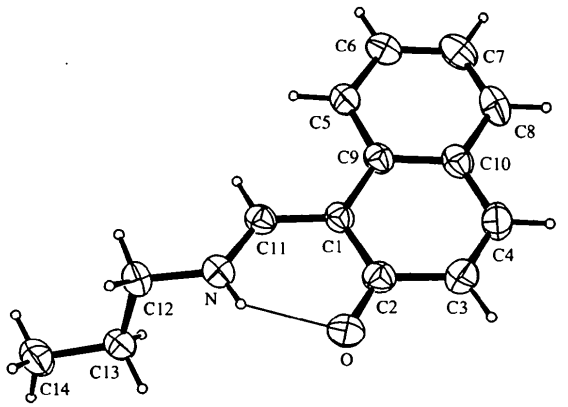


Fig. 1. An *ORTEP*II (Johnson, 1976) view of the molecule with displacement ellipsoids drawn at the 30% probability level.

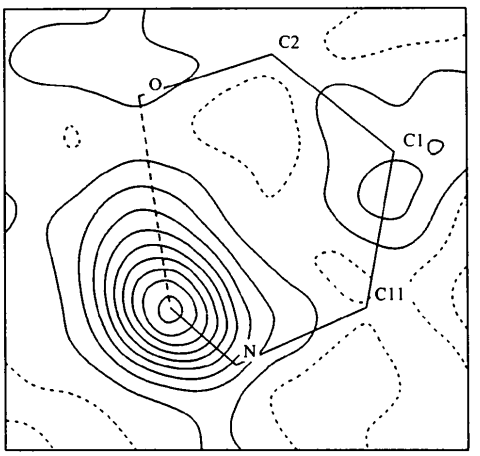


Fig. 2. The contour difference Fourier map for the least-squares plane through the chelate atoms O, N, C1, C2 and C11 showing the position of the H1N atom (solid lines) and revealing the presence of intramolecular N—H···O hydrogen bonding. Contours are drawn from −0.20 to +0.60 e Å^{-3} at intervals of 0.06 e Å^{-3}.

The C2=O bond [1.277 (2) Å] was determined to be of bond order 1.5 from the values of the single and double C—O bonds (Allen *et al.*, 1987). This, along with the very short C3=C4 bond [1.343 (3) Å], suggests the presence of a significant quinoidal effect. This quinoidal effect is probably the consequence of the naphthaldimine ligands endeavouring to retain the same arrangement of bond lengths as is found in the naphthalene moiety as a result of its D_{2h} crystallographic symmetry. From the X-ray diffraction experiment, we were only able to detect the existence of the keto tautomer.

Experimental

The title compound (I) was prepared by stirring equimolar methanol solutions of 2-hydroxy-1-naphthaldehyde and *n*-propylamine and recrystallized from *n*-heptane.

Crystal data

$C_{14}H_{15}NO$
M_r = 213.28
Monoclinic
$P2_1/c$
a = 10.1646 (7) Å
b = 8.8048 (6) Å
c = 13.157 (1) Å
β = 96.327 (6)°
V = 1170.3 (1) Å^3
Z = 4
D_x = 1.210 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 35 reflections
θ = 10.00–19.50°
μ = 0.07 mm^{-1}
T = 295 K
Irregular block
0.65 × 0.65 × 0.26 mm
Pale yellow

Data collection

Phillips PW1100 (Stoe upgraded) diffractometer
ω scans
Absorption correction: none
2846 measured reflections
2397 independent reflections
1232 observed reflections [$I_{net} > 2.0\sigma(I_{net})$]
R_{int} = 0.037
θ_{max} = 27.00°
h = −13 → 12
k = 0 → 11
l = 0 → 16
4 standard reflections
frequency: 60 min
intensity decay: 2.9%

Refinement

Refinement on F
R = 0.036
wR = 0.058
S = 1.13
1232 reflections
145 parameters
H atoms riding
$w = 1/[\sigma^2(F) + 0.002F^2]$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.12 e Å^{-3}
$\Delta\rho_{min}$ = −0.10 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
O	0.3468 (2)	0.1387 (2)	0.6558 (1)	0.069 (1)
N	0.5766 (2)	0.0274 (2)	0.7168 (1)	0.058 (1)
C1	0.3851 (2)	−0.0177 (2)	0.8035 (1)	0.048 (1)
C2	0.3021 (2)	0.0675 (2)	0.7294 (2)	0.055 (1)
C3	0.1626 (2)	0.0717 (3)	0.7401 (2)	0.066 (1)
C4	0.1119 (2)	0.0020 (3)	0.8178 (2)	0.067 (1)
C5	0.4068 (2)	−0.1694 (2)	0.9677 (1)	0.055 (1)
C6	0.3500 (2)	−0.2353 (3)	1.0465 (2)	0.066 (1)
C7	0.2149 (2)	−0.2264 (3)	1.0524 (2)	0.075 (2)
C8	0.1375 (2)	−0.1490 (3)	0.9782 (2)	0.072 (1)
C9	0.3306 (2)	−0.0899 (2)	0.8892 (1)	0.049 (1)
C10	0.1922 (2)	−0.0796 (2)	0.8952 (2)	0.056 (1)
C11	0.5198 (2)	−0.0339 (2)	0.7908 (1)	0.050 (1)
C12	0.7120 (2)	0.0001 (3)	0.6962 (2)	0.061 (1)
C13	0.7186 (2)	−0.0956 (3)	0.6015 (2)	0.061 (1)
C14	0.8581 (2)	−0.1106 (3)	0.5731 (2)	0.082 (2)

Table 2. *Selected geometric parameters (Å, °)*

O—C2	1.277 (2)	C5—C6	1.369 (3)
N—C11	1.303 (2)	C5—C9	1.408 (3)
N—C12	1.452 (3)	C6—C7	1.386 (3)
C1—C2	1.429 (3)	C7—C8	1.366 (4)

C1—C9	1.455 (3)	C8—C10	1.418 (3)
C1—C11	1.406 (3)	C9—C10	1.421 (3)
C2—C3	1.441 (3)	C12—C13	1.510 (3)
C3—C4	1.343 (3)	C13—C14	1.513 (3)
C4—C10	1.427 (3)	N—H1N	0.775
C11—N—C12	125.3 (2)	C6—C7—C8	118.9 (2)
C2—C1—C9	120.8 (2)	C7—C8—C10	121.5 (2)
C2—C1—C11	118.8 (2)	C1—C9—C5	124.1 (2)
C9—C1—C11	120.4 (2)	C1—C9—C10	118.6 (2)
O—C2—C1	122.9 (2)	C5—C9—C10	117.3 (2)
O—C2—C3	119.8 (2)	C4—C10—C8	121.7 (2)
C1—C2—C3	117.3 (2)	C4—C10—C9	119.0 (2)
C2—C3—C4	121.8 (2)	C8—C10—C9	119.4 (2)
C3—C4—C10	122.4 (2)	N—C11—C1	124.4 (2)
C6—C5—C9	121.5 (2)	N—C12—C13	112.1 (2)
C5—C6—C7	121.5 (2)	C12—C13—C14	112.4 (2)
N—C12—C13—C14	173.9 (2)	O—C2—C3—C4	−178.1 (3)
C5—C9—C10—C4	179.1 (2)	C1—C9—C10—C8	−179.9 (2)
C11—N—C12—C13	107.8 (2)	C12—N—C11—C1	−173.5 (2)
C2—C1—C9—C5	−176.9 (2)	C11—C1—C9—C5	4.8 (1)
C11—C1—C9—C10	−175.6 (2)	C9—C1—C11—N	−179.6 (2)

All non-H atoms were refined by anisotropic full-matrix least squares. H atoms were treated as riding atoms with C—H = 0.95 Å except for the one involved in the intramolecular N—H···O hydrogen bond which was found from a difference Fourier map. All H atoms were included in the structure-factor calculations with isotropic displacement parameters set to 1.2 × U_{eq} of the atom to which they are bonded. Owing to the severe extinction, the reflection 100 was omitted from the least-squares refinement.

Data collection: *STADI4* (Stoe, 1995*a*). Cell refinement: *STADI4*. Data reduction: *X-RED* (Stoe, 1995*b*). Program(s) used to solve structure: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to refine structure: *NRCVAX*. Molecular graphics: *NRCVAX*. Software used to prepare material for publication: *NRCVAX*.

The authors are grateful for funding from the Ministry of Science and Technology, Republic of Croatia.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1185). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 2575–2578

3,4,5,6-Tetra-*O*-benzyl-*cis*-1,2-*O*-cyclohexylidene *myo*-Inositol

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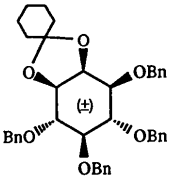
(*Received 28 November 1995; accepted 29 April 1996*)

Abstract

The inositol ring in $C_{40}H_{44}O_6$ is in a chair conformation with the O atom at C2 in the expected axial position and the other five O atoms in equatorial positions. The ring is twisted with one approximate twofold axis retained through the mid-points of the C2—C3 and C5—C6 bonds.

Comment

3,4,5,6-Tetra-*O*-benzyl-*cis*-1,2-*O*-cyclohexylidene *myo*-inositol, (1), is an important intermediate in the syntheses of inositol phosphates and analogues, including *myo*-inositol 1-phosphate (Kiely, Abruscato & Baburao, 1974), *myo*-inositol 1-phosphorothioate (Baker, Billington & Gani, 1991), *myo*-inositol 2-phosphate (Billington, 1993) and *myo*-inositol 1,2-bisphosphate (Spiers *et al.*, 1996). In the presence of acid, the acetal group of (1) cleaves to give 3,4,5,6-tetra-*O*-benzyl *myo*-inositol, the 2-hydroxy position of which is more reactive than the 1-position, a selectivity which is exploited in many of the aforementioned syntheses.



(1)

The biologically important parent compound *myo*-inositol has been analysed by X-ray diffraction, both in the absence (Rabinowitz & Kraut, 1964) and presence of two molecules of water (Lomer, Miller & Beevers, 1963). Both determinations showed the cyclohexane ring to exist in the chair conformation with one of the six hydroxyl groups axial and the others equatorial (1*a*/5*e*). The distortion of the ring from a perfect chair was small in both cases; this was also observed in the fully protected derivatives, 1,2,3,4,5,6-