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MOLECULAR AND ELECTRONIC STRUCTURE OF THE DEHYDROALANINE DERIVATIVES: THE CYCLIC DIPEPTIDE OF DEHYDROPHENYLALANINE

D. AJO'[a*], M. CASARIN[a], R. BERTONCELLO[b], V. BUSETTI[c],
H.C.J. OTTENHEIJM[d] and R. PLATE[d]

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[a] Istituto di Chimica e Tecnologia dei Radioelementi del C.N.R., Corso Stati Uniti 4, 35100 PADOVA, Italy; [b] Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Universita' di Padova, Via Loredan 4, 35131 PADOVA, Italy; [c] Dipartimento di Chimica Organica, Universita' di Padova, Via Marzolo 1, 35131 PADOVA, Italy; [d] Department of Organic Chemistry, University of Nijmegen, Toernooiveld, 6525 ED NIJMEGEN, The Netherlands.

Abstract - The molecular structure of the cyclic dipeptide of dehydrophenylalanine [3,6-bis(phenylmethylene)-piperazine-2,5-dione] has been determined from three dimensional X-ray data. $C_{18}H_{14}N_2O_2$ is monoclinic, space group C2/c, with Z=12 in a cell of dimensions a=40.774(1), b=6.237(2), c=17.731(3) Å, β=107.76(5)°. Molecules are approximately planar as far as the piperazinedione ring is concerned, and they are linked in two series of hydrogen-bonded ribbons. The vapour phase He(I) and He(II) photoelectron spectra are also presented. Their assignment is proposed by comparison with related molecules and supported by semiempirical quantum mechanical calculations. Analogies and differences with respect to the photoelectron results of the cyclic dipeptide of dehydroalanine and corresponding acyclic compounds are discussed.

INTRODUCTION

α,β-unsaturated amino acid derivatives (Fig. 1) are present in many natural peptides, several of which exhibit biological activities[1,2]. The isolation of these dehydropeptides has led to a resurgence of interest in the chemistry of dehydroamino acids. In this context, the biosynthesis of dehydropeptides has also acquired new significance. The α,β-double bond in dehydroaminoacid derivatives, present in addition to the amino and carboxy groups, represents the introduction of a third reactive function into the molecule. Moreover, it renders this class of compounds particularly interesting because of their unusual conformational and electronic features.

In previous papers we reported upon the electronic structure [by photoelectron (PE) spectroscopy] of N-acetyldehydroalanine (dehydro-Ala-OH, Fig. 1a: $R_1 = R_2 = H$; $R_3 = OH$)[3], N-acetyldehydrophenylalanine (dehydro-Phe-OH, Fig. 1a: $R_1 = C_6H_5$, $R_2 = H$, $R_3 = OH$)[4] and several ethyl esters (Fig. 1a: $R_1 = H, CH_3, C_6H_5$; $R_2 = H, CH_3$; $R_3 = OC_2H_5$)[5]. In particular, these studies evidentiated the relevant interaction between "semilocalized" π_N and π_{CC} MOs (giving rise to $\pi^{\pm}_{NCC}$ combinations) which depends on both molecular conformation and nature of the β-substituent. In order to distinguish between conformational[2-11] and electronic[3-5] effects on the structure of dehydro aminoacid derivatives, PE investigation of more rigid systems, e.g. cyclic dehydrodipeptides, appeared particularly suited. Interestingly, several cyclic dehydrodipeptides - e.g. albonoursin[12] and roquefortine[13] - exhibit biological and pharmacological properties, whereas others have been used for asymmetric hydrogenation[14]. Therefore, we investigated recently[15] the

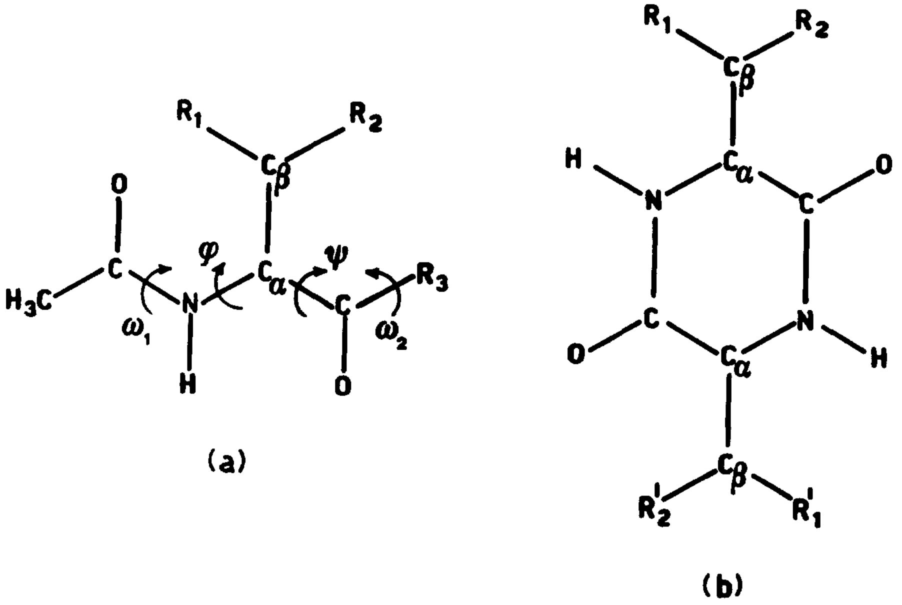

Fig. 1: General structural formula of acyclic (a) and cyclic (b) dehydroalanine derivatives quoted in the present paper.

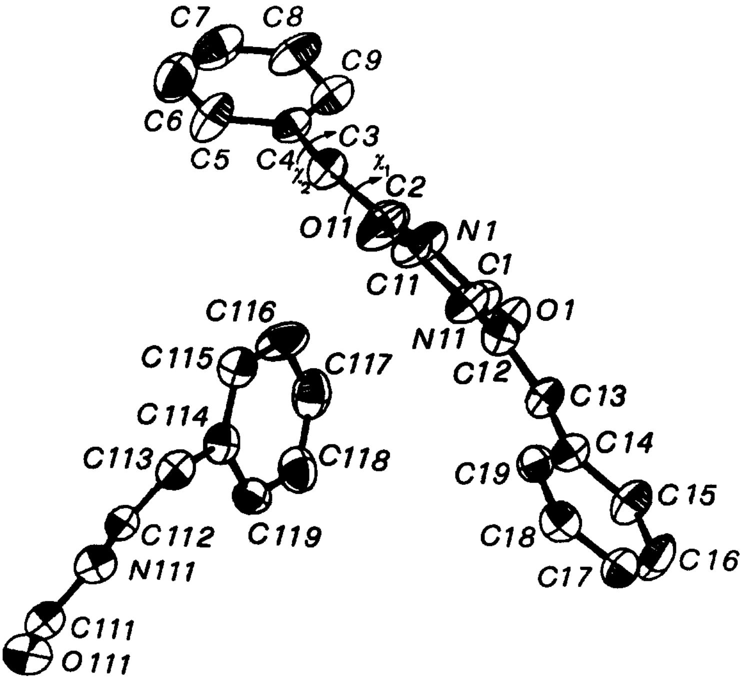

Fig. 2: ORTEP projection onto the xz plane, atom numbering scheme and relevant torsion angles.

molecular and electronic structure of the cyclic dipeptide of dehydroalanine [cyclo(dehydro-Ala)$_2$] (Fig. 1b: $R_1 = R_1' = R_2 = R_2' = H$): the results of this study pointed to a very similar interaction extent, between the orbitals mainly localized on nitrogen and vinyl group, in cyclo(dehydro-Ala)$_2$ and the acyclic corresponding compound dehydro-Ala-OH.

Here we present a study of the molecular, crystal and electronic structure of the cyclic dipeptide of dehydrophenylalanine [cyclo(dehydro-Phe)$_2$, Fig. 1b: $R_1 = R_1' = C_6H_5$; $R_2 = R_2' = H$]*. The electronic structure has been derived from the results of both He(I) and He(II) PE investigations and semiempirical quantum mechanical INDO/S calculations.

RESULTS AND DISCUSSION

X-ray structure: final positional parameters are reported in Table 1. Bond distances and angles are shown in Table 2 and the numbering scheme of the atoms is reported in the ORTEP projection (Fig. 2). Twelve molecules are to be arranged in the unit cell; among them, eight (hereafter **A**) are in the eight general positions of the space group C2/c; the remaining four are made of eight half molecules (**B**) linked in pairs (through the inversion centers at 1/4,1/4,0; 3/4,1/4,1/2; 3/4,3/4,0;1/4,3/4,1/2) to the half ones related by the C-centering symmetry (Fig.3). Bond distances are within the usual range for dehydroamino acid derivatives: in particular the N-C_α bond length ranges from 1.389(8)Å (one half of molecule **A**) to 1.423(9)Å (molecule **B**), to be compared with the reported ones of dehydro-Ala-OH [1.409(5)Å][6], dehydro-Phe-OH [1.438(6)Å][4] and cyclo(dehydro-Ala)$_2$ [1.39(2)Å][15]. Both kinds of molecules are approximately planar as far as the piperazinedione ring is concerned [maximum deviation 0.015(7)Å for molecule **B**, 0.101(7)Å for molecule **A**]. A significant deviation from planarity is observed for the styryl moiety: the absolute value of the χ_2 torsion angle ranges from 18° (one half of molecule **A**) to 43° (molecule **B**); the variation in bond angles is correlated: N-C_α-C_β from 127.5(5) to 123.8(6)° and C_α-C_β-C_γ from 132.8(6) to 129.1(6)°; there are not significantly short distances between amidic and phenyl hydrogen atoms [H.N(1)-H.C(9) = 2.49(7), H.N(11)-H.C(19) = 2.26(6), H.N(111)-H.C(119) = 2.29(9)Å]. The presence of different conformations in the crystal structure of the same molecule suggests a relevant conformational flexibility.

Crystal packing is given in Fig. 3. Molecules **A** are stacked along the c axis, displaced by $(\vec{a}/2 + \vec{b}/2)$ and interleaved by the **B** stacks. The C_α-C_α axes of these two kinds of molecules are almost perpendicular to each other (86.7° between them).

Both **A** and **B** molecules are linked in infinite ribbons by hydrogen bonds (Fig. 4) [O'(11)-N(1) = 2.862(6)Å; O'(11)-H.N(1)-N(1) = 166(4)°; O(1)-N'(11) = 2.853(6)Å; O(1)-H.N'(11)-N'(11) = 158(4)°; O(111)-N"(111) = 2.929(6)Å; O(111)-H.N"(111)-N"(111) = 155(4)°; the single prime refers to molecule at x,y-1,z; the double one refers to molecule at 1/2-x,1/2-y,-z]. Six-membered rings closed by hydrogen bonds are planar: the maximum and average deviations from planarity are 0.080 and 0.055Å, respectively for molecules **A**; 0.104 and 0.084Å for molecules **B**; these values are to be compared with the average value (0.03Å) of cyclo(dehydro-Ala)$_2$[15].

Photoelectron Spectra: He(I) and He(II) PE spectra of the title compound are shown in Figs. 5a and 5b, respectively. In the first spectral region (8.0-10.5 eV ca.) two bands (labeled A and B) are present at 8.39 and 9.49 eV, respectively. Band B exhibits a relevant shoulder S (9.90 eV) on its higher IE side. In this region we expected eight ionizations: four from the dimethylenepiperazine-

* 3,6-bis(phenylmethylene)-piperazine-2,5-dione

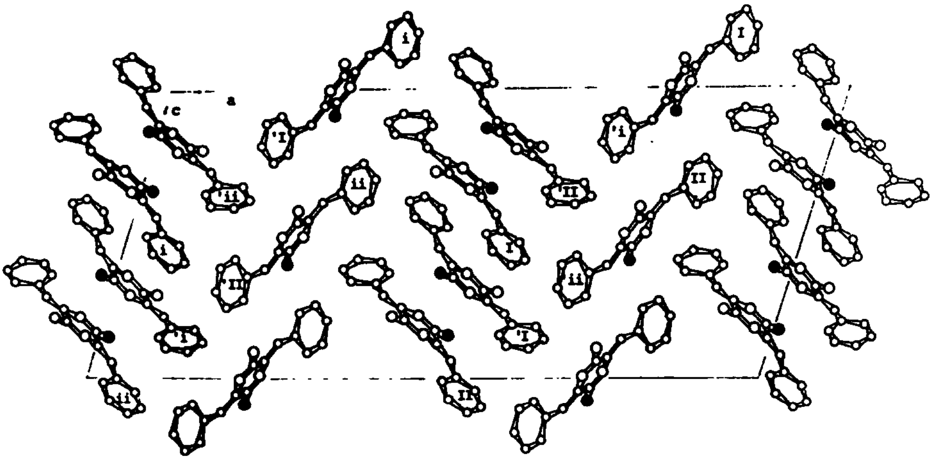

Fig. 3: Crystal packing onto the xz plane. Symmetry code:

i	x, y, z	'i	$\bar{x}$, $\bar{y}$, $\bar{z}$
I	1/2+x, 1/2+y, z	'I	1/2-x, 1/2-y, $\bar{z}$
ii	x, $\bar{y}$, 1/2+z	'ii	$\bar{x}$, y, 1/2-z
II	1/2+x, 1/2-y, 1/2+z	'II	1/2-x, 1/2+y, 1/2-z.

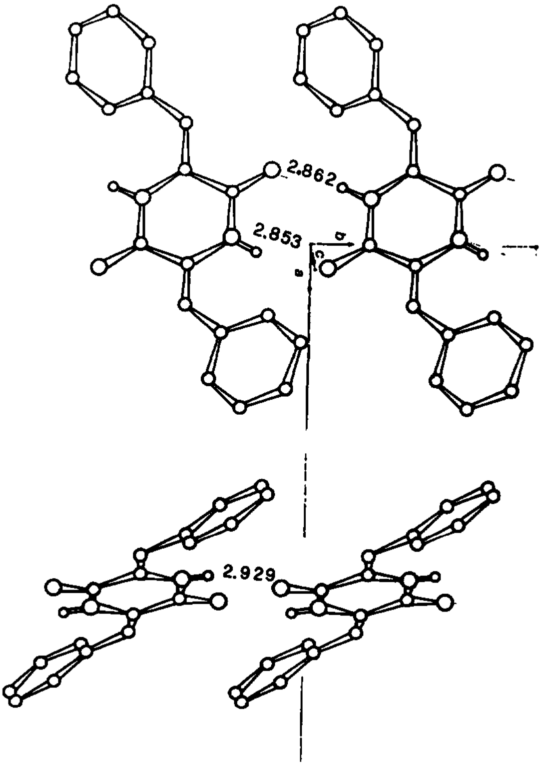

Fig. 4: Hydrogen-bond network.

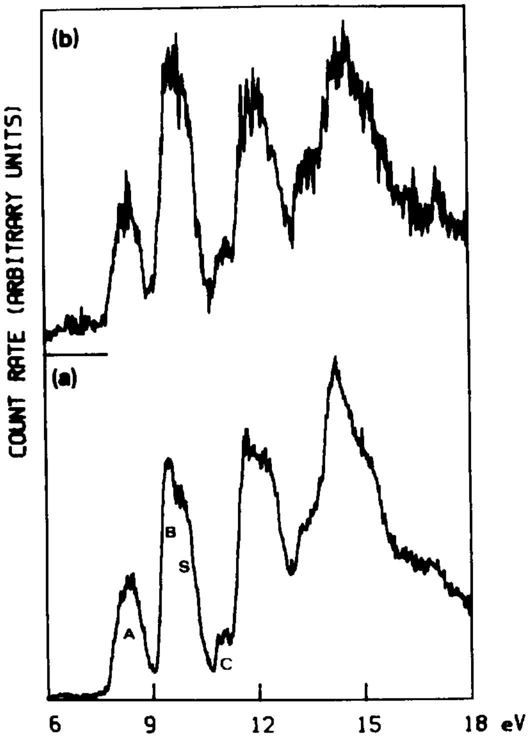

Fig. 5.: He(I) (a) and He(II) (b) PE spectra of cyclo(dehydro-Phe)$_2$.

dione system [9.1 and 10.4 eV in cyclo(dehydro-Ala)$_2$][15] and four from the two phenyl groups [in styrene the first two ionizations lie at 8.49 (π_1) and 9.27 eV (π_2)][16]. The first band C (11.1 eV) of the higher IE region (IE>10.5 eV) is partially hidden by a very intense band at higher IE.

The comparison between the relative intensity of bands A and B (1:3) suggests that the former includes two ionizations, whose assignment to the π_1-like ionizations from both styryl groups is straightforward: the π_1-like MOs can be regarded as arising from the interaction between the two π_1 styryl MOs and the amidic (mainly localized on the nitrogen atoms) π systems [labeled $(\pi^-_{NCC})^{\pm}$ in cyclo(dehydro-Ala)$_2$[15]]: they will be referred to as $(\pi^-_{NCC,Ph1})^{\pm}$. Consistently, we ascribe band B to the superimposition of six ionizations, namely: two π_2-like (from virtually non interacting phenyl MOs) ionizations $(\pi_{Ph2})^{\pm}$; two π_3-like MOs (10.55 eV in styrene[16]) which are the counterpart of the π_1-like ones and will be referred to by the same label $(\pi^-_{NCC,Ph3})^{\pm}$; n_o^+ and n_o^- combinations of in-plane oxygen lone pairs.

Quite obviously, $(\pi_{Ph2})^{\pm}$ are expected to lie at lower IE than $(\pi^-_{NCC,Ph3})^{\pm}$ and they are easily ascribed to band B (9.49 eV, to be compared with 9.27 eV in styrene[16]), while both ionizations from $(\pi^-_{NCC,Ph3})^{\pm}$ are certainly included in the intense shoulder S together with $n_o^{\pm}$ "lone-pairs".

The He(II) spectrum supports our assignments since band B increases in relative intensity with respect to band A under He(II) radiation, as expected for bands including ionizations from MOs highly localized on oxygen atoms[17]; furthermore, the B-S band system exhibits a more symmetrical shape under He(II) radiation, which confirms the inclusion of $n_o^{\pm}$ ionizations within the shoulder S. Finally a relative increase in intensity is observed for band C too; this suggests the assignment of this band to a π MO $(\pi^+_{NCC,Ph})^+$, reminiscent of $(\pi^+_{NCC})^+$ in cyclo(dehydro-Ala)$_2$ which markedly involves oxygen atoms[15]; moreover, band C exhibits a vibrational progression

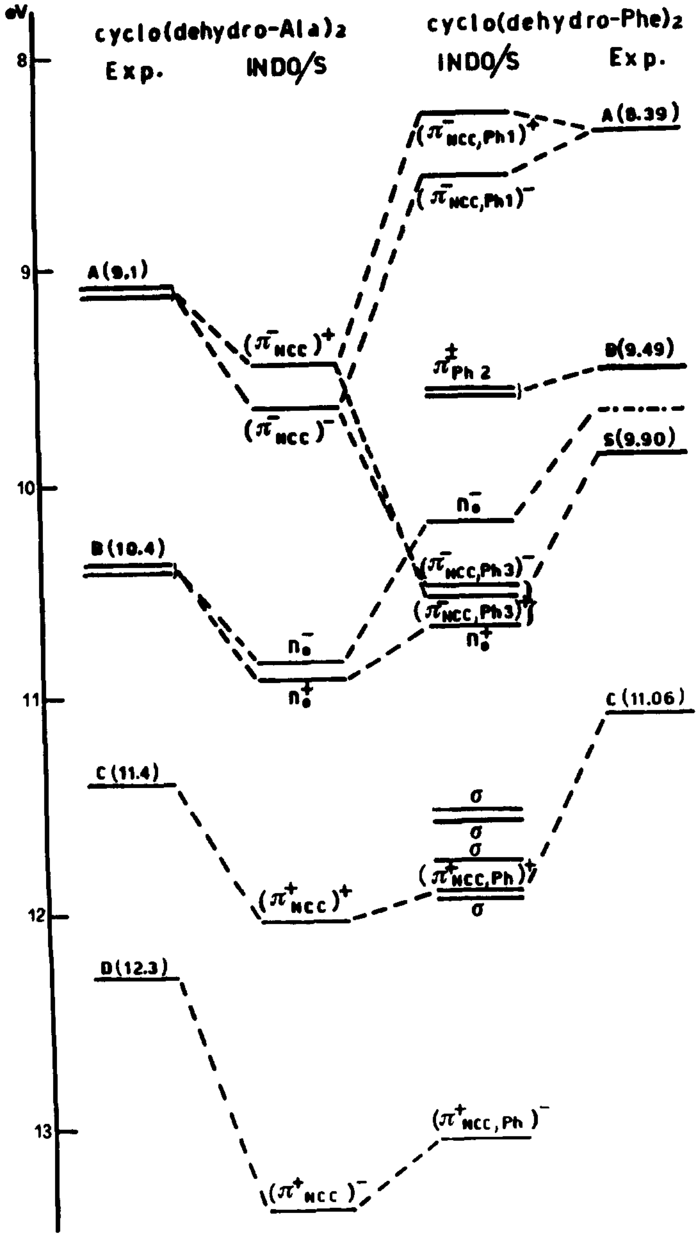

Fig. 6: Correlation diagram for cyclo(dehydro-Ala)$_2$ and cyclo(dehydro-Phe)$_2$ based on INDO/S results.

analogous to that previously observed, but not discussed, in the band C of the cyclo(*dehydro*-Ala)$_2$ spectrum (1600 cm^{-1} ca.).

It is noteworthy that the shoulder S lies at much higher IE than the corresponding band A in cyclo(*dehydro*-Ala)$_2$, while the opposite should be expected on the basis of the inductive effect only from the phenyl groups. This is evidence of the major role played by conjugative interactions between π MOs of phenyl and dimethylenepiperazinedione rings in determining the whole electronic structure.

A further support to the detailed picture derived from the PE results can be provided by quantum mechanical calculations. *Ab initio* calculations, previously used in the investigation of cyclo(*dehydro*-Ala)$_2$[15], are not suitable in the present study, due to the larger molecular size of the title molecule; on the other hand, *ab initio*[15] and semiempirical INDO/S[18] calculations of cyclo(*dehydro*-Ala)$_2$ gave very similar results.

Therefore we report here the results of INDO/S calculations of cyclo(*dehydro*-Phe)$_2$. Geometrical parameters were obtained from the X-ray internal coordinates by symmetrization to the C_{2h} point group (as noted above, the X-ray results suggest the presence of several quasi-planar conformers in the vapour phase).

The INDO/S correlation diagram of cyclo(*dehydro*-Ala)$_2$ and cyclo(*dehydro*-Phe)$_2$ is shown in Fig. 6, together with experimental IEs. The experimental trend is well reproduced, apart from overall shift towards higher IEs; on the other hand, this is observed for cyclo(*dehydro*-Ala)$_2$ too, where the assignment are straightforward.

Although the distinctive feature of cyclo(*dehydro*-Phe)$_2$ is the relevant $\pi_{NCC,Ph}$ interaction, the pattern derived from the quantum mechanical calculations on the title compound is similar to that of cyclo(*dehydro*-Ala)$_2$ as far as the π_{NCC} interaction is concerned. Moreover, the analysis of the eigenvectors shows that all of the π MOs (except $\pi^{\pm}_{Ph}$), in particular the quasi-degenerate HOMOs, have comparable contributions from π_N, π_{CC} centers [like in cyclo(*dehydro*-Ala)$_2$]. It is noteworthy that these features are common to the two cyclic systems and *dehydro*-Ala-OH[3] (or *dehydro*-Ala-OC$_2$H$_5$)[5], but they are absent in acyclic *dehydro*-Phe derivatives.

CONCLUSIONS

The PE results of cyclo(*dehydro*-Phe)$_2$ stress the role of conjugative interactions between π MOs of phenyl and piperazinedione rings, in addition to those within the enamino moiety. The actual extent of the $\pi_{NCC,Ph}$ interactions is much better evidentiated by the above results - when compared with those of cyclo(*dehydro*-Ala)$_2$ - than by comparison between corresponding acyclic molecules (*dehydro*-Ala-R and *dehydro*-Phe-R, R = OH, OC$_2$H$_5$) where important conformational effects - in particular, as the φ torsion angle is concerned - are present.

EXPERIMENTAL

Crystal data: $C_{18}H_{14}N_2O_2$, M=290.3. Crystals of the title compound, prepared according to ref. 19, are monoclinic, space group C2/*c*, *a*=40.774(1), *b*=6.237(2), *c*=17.731(3)Å, β=107.76(5)°, *V*=4294(2)Å^3, *Z*=12, D_m=1.36 (by flotation in H$_2$O/KI solution), D_c=1.347gcm^{-3}, F(000)=1824, MoK$_\alpha$ radiation (monochromatized by a graphite plate), λ=0.71069Å, μ(MoK$_\alpha$)=0.83cm^{-1}.

Solution and refinement of the structure: intensity data were measured on a Philips PW 1100 four circles diffractometer (graphite monochromatized MoK$_\alpha$ radiation). For data collection a crystal 0.15 x 0.05 x 0.80 mm was used, ϑ-2ϑ scan mode, scan width 1.20°, scan speed 0.030°s^{-1}, background measured for 10s at each extremity, ϑ 1 to 24°, 3 standard intensity reflections ($\overline{10}$ 0 4),

$(\bar{8}\ 0\ \bar{2})$, $(10\ \bar{2}\ \bar{2})$ measured at 3h intervals: no significant variations. Unit cell: least square refinement of 22 values, $18<\vartheta<22^\circ$; Lorentz polarization correction, no adsorption correction. Of 3373 independent collected reflections, 1486 had $I>3\sigma(I)$. $R_{int}=0.011$.

The structure was solved by direct methods; E map revealed all non-hydrogen atoms. Full matrix least-square refinement (on F), unit weights. All hydrogen atoms localized on a difference map and refined in the last cycle of least squares. Residual peaks in final difference map from -0.23 to +0.23 eÅ^{-3}. The refinement converged to R=0.061. Calculations were performed on a Cyber 76 computer by the SHELX[20] and MULTAN78[21] programs for crystal structure determination. All atomic scattering factors were taken from ref. 22. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 45,290.

Photoelectron Spectra: He(I) and He(II) excited PE spectra were recorded on a Perkin-Elmer PS-18 spectrometer modified by inclusion of a hollow-cathode discharge lamp giving high photon flux at the He(II) wavelengths (Helectros Developments). The spectrometer was connected on line with a MINC 23 computer (DEC). Data acquisition was carried out by several sweeps over 500 distinct channels. Typical sweep time amounts to 5-10 min. The spectra were calibrated by reference to admixed inert gases (Ar,Xe) and to 1s^{-1} He self-ionization.

Quantum mechanical calculations: quantum mechanical calculations were performed within the INDO/S scheme[23,24]. The computed eigenvalues can be related to the measured ionization energies (IEs) through Koopmans' approximation[25].

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Table 1. Fractional atomic coordinates (x10^4 for non-hydrogen atoms, x10^3 for hydrogen atoms) and B (Å^2) equivalent temperature factors; e.s.d.'s in parentheses.

	x	y	z	B_{eq}
O(1)	95(1)	753(6)	3581(2)	3.3(1)
N(1)	-368(1)	2522(8)	2810(3)	3.0(1)
C(1)	-57(2)	2467(10)	3383(3)	3.2(2)
C(2)	-573(2)	4329(9)	2577(3)	3.0(2)
C(3)	-895(2)	4344(11)	2071(4)	3.4(2)
C(4)	-1106(1)	2600(10)	1625(3)	3.1(2)
C(5)	-1456(2)	2658(13)	1547(4)	4.8(2)
C(6)	-1673(2)	1048(17)	1133(5)	5.9(3)
C(7)	-1537(2)	-560(14)	813(5)	5.3(3)
C(8)	-1200(2)	-701(12)	881(4)	4.8(2)
C(9)	-980(2)	906(11)	1304(4)	3.8(2)
O(11)	-568(1)	8105(6)	2660(3)	4.4(1)
N(11)	-108(1)	6356(8)	3439(3)	3.1(1)
C(11)	-417(2)	6410(10)	2885(4)	3.1(2)
C(12)	78(1)	4522(9)	3774(3)	2.9(2)
C(13)	357(2)	4420(10)	4402(4)	3.1(2)
C(14)	546(1)	6020(9)	4961(3)	2.9(2)
C(15)	871(2)	5504(13)	5457(4)	4.2(2)
C(16)	1059(2)	6889(13)	6028(4)	4.7(3)
C(17)	924(2)	8821(13)	6143(4)	4.4(2)
C(18)	601(2)	9408(12)	5670(4)	4.0(2)
C(19)	414(2)	8014(10)	5076(4)	3.4(2)
O(111)	2447(1)	-1114(7)	763(3)	4.3(1)
N(111)	2603(1)	549(9)	-195(4)	3.4(2)
C(111)	2471(2)	556(10)	414(4)	3.2(2)
C(112)	2653(1)	2359(10)	-636(4)	2.8(2)
C(113)	2802(2)	2265(11)	-1196(4)	3.2(2)
C(114)	2956(2)	402(10)	-1475(4)	3.4(2)
C(115)	2908(2)	123(13)	-2263(5)	4.3(3)
C(116)	3056(2)	-1596(13)	-2537(5)	4.9(3)
C(117)	3256(2)	-3034(12)	-1999(5)	4.8(3)
C(118)	3313(2)	-2733(13)	-1221(5)	4.6(3)
C(119)	3163(2)	-1065(12)	-938(4)	3.7(2)
H.N(1)	-45(1)	126(8)	267(3)	
H.C(3)	-100(1)	569(9)	195(3)	
H.C(5)	-158(1)	393(8)	175(3)	
H.C(6)	-187(2)	147(17)	102(6)	
H.C(7)	-166(1)	-180(9)	62(3)	
H.C(8)	-109(1)	-188(10)	58(3)	
H.C(9)	-74(1)	85(9)	122(3)	
H.N(11)	0(1)	751(8)	346(3)	
H.C(13)	46(1)	309(9)	448(3)	
H.C(15)	94(1)	410(9)	536(3)	
H.C(16)	130(1)	636(9)	633(3)	
H.C(17)	107(1)	981(9)	667(3)	
H.C(18)	49(1)	1077(8)	578(3)	
H.C(19)	19(1)	862(8)	473(3)	
H.N(111)	264(1)	-64(10)	-41(4)	
H.C(113)	281(1)	354(9)	-150(3)	
H.C(115)	279(1)	117(9)	-257(3)	
H.C(116)	300(1)	-179(9)	-310(4)	
H.C(117)	336(1)	-435(10)	-221(4)	
H.C(118)	348(1)	-369(11)	-85(4)	
H.C(119)	320(1)	-75(9)	-42(3)	

Table 2. Bond distances (Å) and angles (°); e.s.d.'s in parentheses.

C(1)-O(1)	1.232(7)	C(11)-O(11)	1.227(7)	C(111)-O(111)	1.231(8)
C(1)-N(1)	1.362(7)	C(11)-N(11)	1.341(8)	C(111)-N(111)	1.346(11)
N(1)-C(2)	1.389(8)	N(11)-C(12)	1.401(7)	N(111)-C(112)	1.423(9)
C(2)-C(3)	1.345(9)	C(12)-C(13)	1.329(7)	C(112)-C(113)	1.314(11)
C(3)-C(4)	1.461(8)	C(13)-C(14)	1.451(8)	C(113)-C(114)	1.476(10)
C(4)-C(5)	1.392(9)	C(14)-C(15)	1.386(8)	C(114)-C(115)	1.362(11)
C(5)-C(6)	1.391(12)	C(15)-C(16)	1.373(10)	C(115)-C(116)	1.389(12)
C(6)-C(7)	1.352(14)	C(16)-C(17)	1.366(12)	C(116)-C(117)	1.380(10)
C(7)-C(8)	1.345(12)	C(17)-C(18)	1.378(10)	C(117)-C(118)	1.340(12)
C(8)-C(9)	1.400(9)	C(18)-C(19)	1.399(9)	C(118)-C(119)	1.377(12)
C(9)-C(4)	1.372(9)	C(19)-C(14)	1.395(9)	C(119)-C(114)	1.402(9)
C(1)-C(12)	1.481(8)	C(2)-C(11)	1.475(8)	C(112)-C'(111)	1.491(8)

C(12)-C(1)-O(1)	122.3(5)	C(2)-C(11)-O(11)	121.4(6)	C'(112)-C(111)-O(111)	121.3(6)
O(1)-C(1)-N(1)	120.5(6)	O(11)-C(11)-N(11)	121.7(6)	O(111)-C(111)-N(111)	120.9(6)
C(12)-C(1)-N(1)	117.1(5)	C(2)-C(11)-N(11)	116.9(5)	C'(112)-C(111)-N(111)	117.8(5)
C(1)-N(1)-C(2)	125.5(5)	C(11)-N(11)-C(12)	126.7(5)	C(111)-N(111)-C(112)	126.7(6)
N(1)-C(2)-C(3)	125.5(6)	N(11)-C(12)-C(13)	127.5(5)	N(111)-C(112)-C(113)	123.8(6)
N(1)-C(2)-C(11)	116.8(6)	N(11)-C(12)-C(1)	115.6(5)	N(111)-C(112)-C(111)	115.5(5)
C(3)-C(2)-C(11)	117.6(6)	C(13)-C(12)-C(1)	116.9(5)	C(113)-C(112)-C'(111)	120.7(5)
C(2)-C(3)-C(4)	130.5(6)	C(12)-C(13)-C(14)	132.8(6)	C(112)-C(113)-C(114)	129.1(6)
C(3)-C(4)-C(9)	124.4(6)	C(13)-C(14)-C(19)	124.4(6)	C(113)-C(114)-C(119)	121.0(6)
C(3)-C(4)-C(5)	116.8(6)	C(13)-C(14)-C(15)	118.6(6)	C(113)-C(114)-C(115)	120.1(6)
C(5)-C(4)-C(9)	118.7(6)	C(15)-C(14)-C(19)	116.8(6)	C(115)-C(114)-C(119)	118.8(7)
C(4)-C(5)-C(6)	120.1(7)	C(14)-C(15)-C(16)	122.2(7)	C(114)-C(115)-C(116)	121.1(8)
C(5)-C(6)-C(7)	118.7(8)	C(15)-C(16)-C(17)	120.4(8)	C(115)-C(116)-C(117)	119.2(8)
C(6)-C(7)-C(8)	123.3(8)	C(16)-C(17)-C(18)	119.8(7)	C(116)-C(117)-C(118)	120.1(8)
C(7)-C(8)-C(9)	118.1(8)	C(17)-C(18)-C(19)	119.6(7)	C(117)-C(118)-C(119)	121.6(8)
C(8)-C(9)-C(4)	120.9(7)	C(18)-C(19)-C(14)	121.2(7)	C(118)-C(119)-C(114)	119.2(7)

atoms related by symmetry center are marked by an apex.