

The synthesis and structure of a redox-active cryptand containing both aromatic and phenanthroline units within the macrocyclic structure.

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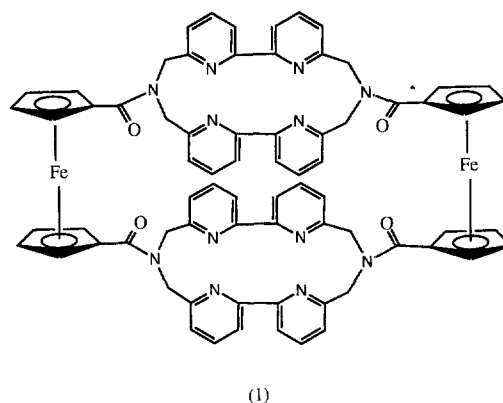
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Abstract

The synthesis of 1,1'(4,5,10,11-dibenzo-6,9-dioxa-3,12,23,26-tetraazatetracyclo[12.8.4.0.0]hexacos-1(22),14,16,18,20,23,25-heptaene-3,12-diylidicarbonyl)ferrocene is reported and its structure, as determined by multinuclear nmr and X-ray diffraction, involves *trans* orientation of the amide carbonyl groups. © 1997 Elsevier Science S.A.

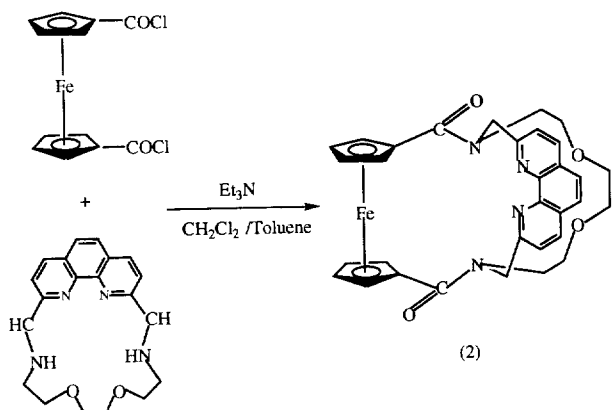
1. Introduction

The synthesis, structure, electrochemistry and complex formation of cryptands containing metallocene units have attracted considerable attention in recent years [1–8]. These redox-active compounds are potentially useful as sensors for the detection and quantitative estimation of metal cations by electrochemical techniques [9] as catalysts in a variety of reactions [10] and as models for electron transfer in biological systems [11]. Some years ago it was shown by Lehn that irradiation of lanthanide complexes of certain cryptands with ultraviolet light led to a red luminescence at 610 nm due to energy transfer from the excited state of bipyridyl units within the cryptand to the guest cation (Eu^{3+} or Tb^{3+}) followed by fluorescence from the $^5\text{D}_0$ and $^5\text{D}_4$ levels of complexed cations [12,13]. Application of this principle to redox-active cryptands enabled us to show that the cryptand **1**

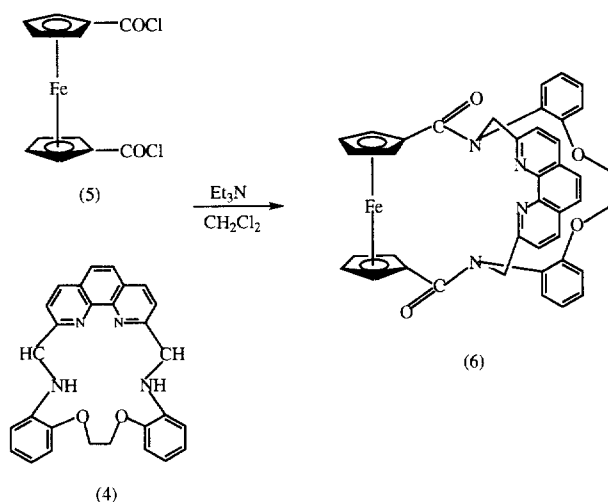


also formed a complex with Eu^{3+} which fluoresced at 620 nm on irradiation with ultraviolet light [14]. Since we have established that electrochemical oxidation of the metallocene unit within redox-active cryptates tend to expel highly charged cations from the cavity [15,16], it was proposed that such a system might form the basis of a photochemical switch, in effect a voltage-regulated optical sensor. Since **1** is particularly difficult to prepare, it was decided to synthesise redox-active cryptands containing the more readily derivatised phenanthroline

unit as the 'photo antenna' for the system. This was achieved successfully with the synthesis of **2**



[17] where the nmr data indicated a *trans* configuration of the carbonyl groups as in earlier studies [4,6,18,19]. Unfortunately, confirmation of the structure by X-ray crystallography has not so far been achieved but synthesis of an analogous cryptand **6** from **4** and **5**



resulted in the isolation of suitable crystals and this paper reports the results of a structural study of **6** by a combination of X-ray crystallography and multinuclear nmr.

2. Results and discussion

The tetraazadioxa macrocycle **4** was synthesised by a reaction of 1,10-phenanthroline-2,9-dicarboxaldehyde with 1,2,7,8-dibenzo-1,8-diamino-3,6-dioxaoctane (see Section 3) and condensed with ferrocene bis-acid chloride **5** to give a 23% yield (after chromatography) of the cryptand **6** with no evidence for the simultaneous for-

mation of the 2:2 dimer as found with aliphatic diaza crowns [20]. A FAB mass spectrum gave an $M + Na^+$ peak at 709 to establish the monomeric structure and an accurate FAB mass spectrum ($M + Na^+$) 709.1514 confirmed the molecular formula as $C_{40}H_{30}FeN_4O_4$. The elemental analysis of the isolated material, however, gave low values for carbon and nitrogen. Careful inspection of the 1H and ^{13}C nmr spectra revealed both water (1 mol) and dichloromethane (0.5 mol) within the material despite careful drying under high vacuum. When the water and CH_2Cl_2 were included in the calculation, the values gave satisfactory agreement with the theoretical figures (see Section 3). The infrared data showed amide carbonyl stretch at 1618 cm^{-1} and the *trans* disposition of the carbonyl groups was confirmed as in previous work [17] by the highly unsymmetrical nature of the 1H data (Table 3) which showed eight separate ferrocene hydrogen signals, six separate signals for the phenanthroline hydrogens, an unassigned multiplet for the hydrogens of the aromatic rings, four NCH hydrogens and four OCH_2 signals. In addition, the ^{13}C spectrum (Table 3) showed two carbonyl signals, eight ferrocene CH signals, two quaternary carbons on the ferrocene rings, six phenanthroline CH signals, six ipso carbons of the phenanthroline ring, two NCH_2 signals, two OCH_2 signals and twelve aromatic (8 CH + 4 ipso) carbon signals. The data of Table 3 was assigned by a combination of DEPT (135), COSY (Fig. 1) and heteronuclear ($^1H/^{13}C$) shift correlation spectroscopy.

Clearly therefore, the molecule prefers a *trans* configuration of the carbonyl groups in solution. Slow evaporation of the deuteriochloroform of the nmr sample over several weeks gave crystals of the cryptand which were suitable for X-ray crystallography. The resultant structure is shown in Fig. 2 and there is no doubt from this picture that the $C=O$ groups are also disposed *trans* to each other in the solid state. This appears to be a general phenomenon in cryptands of this kind and is presumably associated with the minimisation of the dipole moment of the molecule. The distance between the two cyclopentadiene planes is 3.27 Å. These rings are not exactly eclipsed, there being a twist of 19.4° between the closest atoms. Those attached to the cyclopentadiene rings, C1–C6 and C1'–C21 subtend an angle of 92.34° when viewed normal to their planes. A selection of bond distances and bond angles is shown in Table 4. Examination of the two amide functions shows that the system composed of C1'–C20–C21–C22–O4–N4 is the most planar (maximum deviation 0.092 Å) whereas the other (C1–C6–C7–C35–O1–N4) has all atoms coplanar except for C35 with a deviation of 0.21 Å. The remaining features of the molecule are unremarkable except that the aromatic rings are almost parallel to each other but one is much closer to the ferrocene unit than the other thus, confirming the pronounced lack of symmetry observed in the nmr spectra.

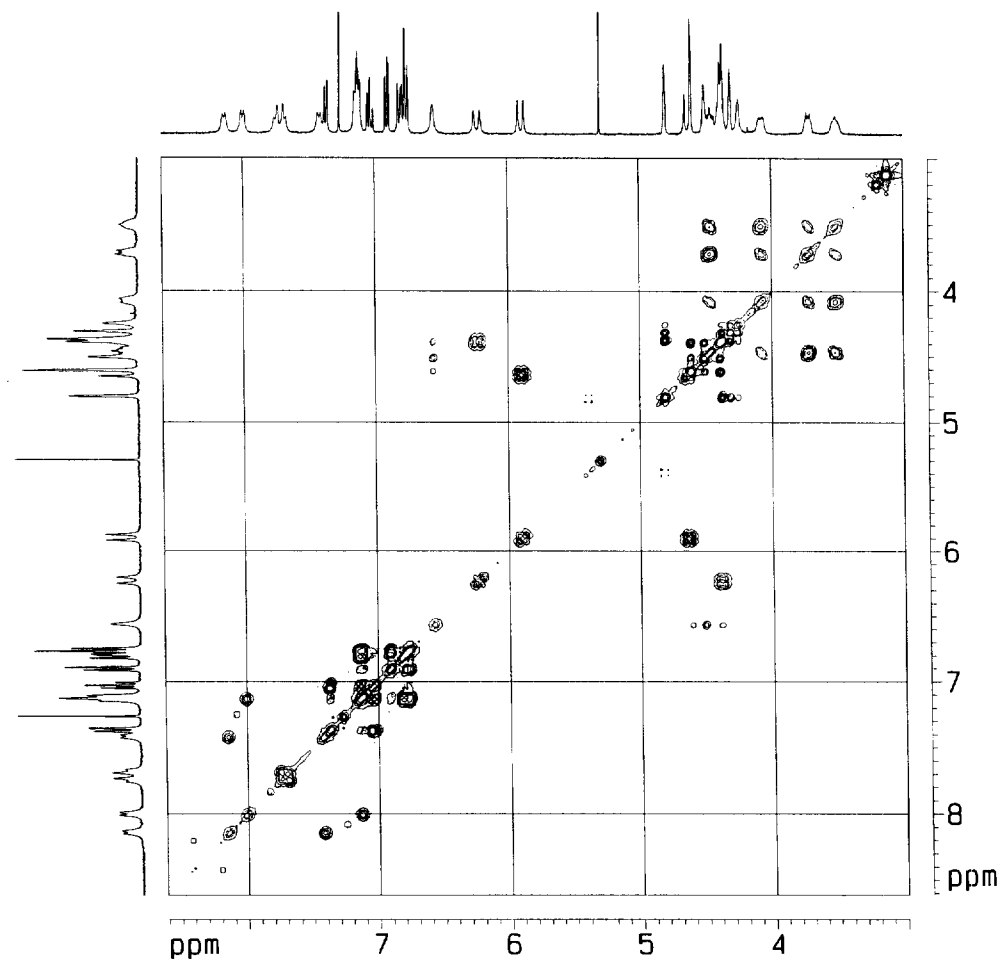


Fig. 1.

The crystal structure contains two molecules of water per ferrocene unit and the two oxygen atoms concerned are not hydrogen bonded to the cryptand but to each

other. There are two hydrogen atoms between them, too close together to be present simultaneously and these were given half occupancy. There were a few peaks on

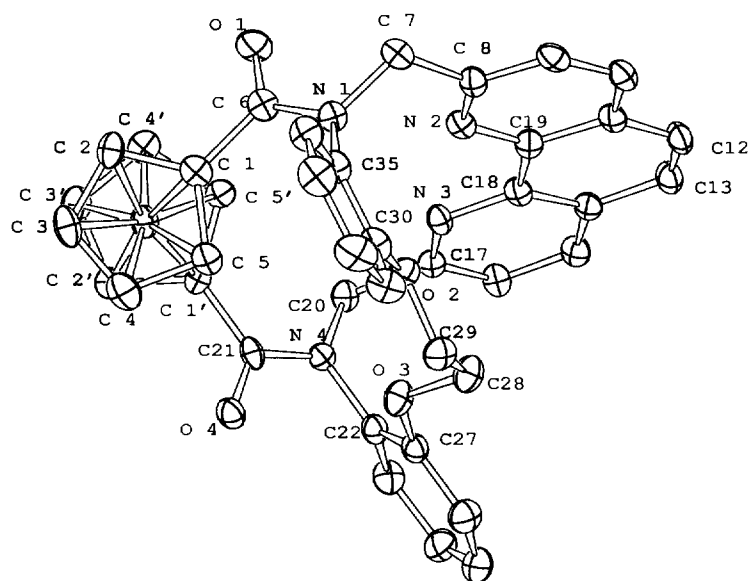


Fig. 2.

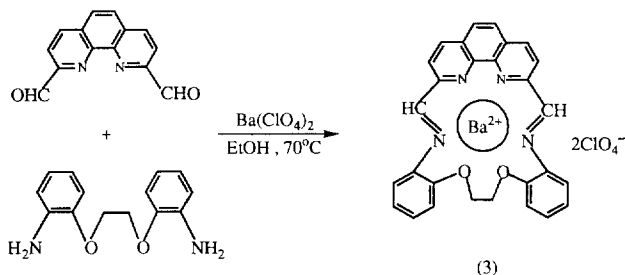
the final ΔF map, about 1 Å from these oxygen atoms but the interbond angles did not correspond to any rational hydrogen-bonded dimer and were therefore not included in the final refinement. Somewhat surprisingly in view of the nmr data, the crystal did not contain any dichloromethane and it must be assumed that the solvent was either not occluded in the crystal or else it evaporated after mounting and/or during irradiation.

In conclusion therefore, it has been shown that the redox-active cryptand containing both aromatic and heteroaromatic units again adopts a *trans* configuration of the carbonyl groups in solution and as the solid. The mobility of the carbonyl groups is demonstrated, however, by complexation with a variety of metal cations in both a 1:1 and 2:1 (L: cation) stoichiometry when a plane of symmetry develops, as shown by nmr, for both types of complex. This will be the subject of a subsequent paper together with a report of the effects of complexation on the redox activity of the host system.

3. Experimental

^1H and ^{13}C nmr spectra were recorded on either Bruker AM360 or Bruker AMX400 spectrometers using CDCl_3 and/or d_6DMSO as solvents.

3.1. Synthesis of the barium complex of 4,5,10,11-dibenzo-6,9-dioxa-3,12,23,26-tetraazatetracyclo[12.8.4.0.0]hexacos-1(22),2,12,14,16,18,20,23,25-nonaene (3)



A solution of 1,10-phenanthroline-2,9-dicarboxaldehyde (0.68 g, 2.86 mmol) and anhydrous barium perchlorate (0.96 g, 2.86 mmol) in dry absolute ethanol (350 ml) was stirred under N_2 at 70°C in a 1 dm³ three-necked flask. A solution of 1,2,7,8-dibenzo-1,8-diamino-3,6-dioxaoctane (0.76 g, 2.86 mmol) in ethanol (350 ml) was then added dropwise over 3 h. During this time a bright yellow precipitate was observed to form which, at the end of the addition, was filtered off and dried under vacuum (0.5 mm) to yield the barium perchlorate complex of the title compound as a yellow solid (1.55 g, 65.5%) with m.p. $> 250^\circ\text{C}$. The ^1H nmr and ^{13}C nmr data (in d_6DMSO) are recorded in Table 1.

3.2. Synthesis of 4,5,10,11-dibenzo-6,9-dioxa-3,12,23,26-tetraazatetracyclo[12.8.4.0.0]hexacos-1(22),14,16,18,20,23,25-heptaene (4)

The barium perchlorate complex (1.55 g, 2 mmol) was stirred with a solution of sodium borohydride (1.9 g, 50 mmol) in absolute ethanol (160 ml) for 8 h. The suspension gradually changed from yellow to a creamy colour. The suspension was filtered and the solid was suspended in benzene (50 ml), heated under reflux for 10 min and the solvent evaporated to give 0.84 g, (94%) of the title compound, m.p. $> 250^\circ\text{C}$. The ^1H nmr and ^{13}C nmr data are recorded in Table 2.

3.3. Synthesis of 1,1'(4,5,10,11-dibenzo-6,9-dioxa-3,12,23,26-tetraazatetracyclo[12.8.4.0.0]hexacos-1(22),14,16,18,20,23,25-heptaene-3,12-diylldicarbonyl) ferrocene (6)

A 1 dm³ three-necked creased round-bottomed flask equipped with a condenser and a mechanical stirrer was flushed with nitrogen and then charged with a solution of 1,1'-bis-(dichlorocarbonyl)ferrocene (0.42 g, 1.34 mmol) dissolved in anhydrous dichloromethane (400 ml). While maintaining the reaction mixture under reflux, a solution of the phenanthroline macrocycle (4, 0.60 g, 1.34 mmol) and triethylamine (1.35 g, 13.37 mmol) dissolved in anhydrous dichloromethane (400 ml) was added dropwise over 6 h. The mixture was concentrated to 200 ml and the organic solution was washed with water (3×250 ml), dried over MgSO_4 and evaporated to leave an orange solid. The crude product was chromatographed on neutral alumina. The first light orange band was collected by eluting with dichloromethane/methanol (99.7%:0.5%) but there was insufficient material to characterise the product. A second orange band was collected by using 0.7%–0.8% methanol in dichloromethane. Removal of solvent under vacuum yielded 210 mg of an orange powder (23%) m.p. $> 250^\circ\text{C}$. Accurate FAB RMM found for $(\text{M} + \text{Na}^+)$ 709.1514; calc. for $\text{C}_{40}\text{H}_{30}\text{FeN}_4\text{NaO}_4$: $\text{M} = 709.1504$. IR (NaCl) ν (cm^{-1}) 1618 (C=O str, amide). Elemental analysis: Calc. for $\text{C}_{40}\text{H}_{30}\text{FeN}_4\text{O}_4$: C, 69.95%; H, 4.41%; N, 8.16%. Found: C, 64.58%; H, 4.49%; N, 7.44%; calc. for $\text{C}_{40}\text{H}_{30}\text{FeN}_4\text{O}_4 \cdot \text{H}_2\text{O} \cdot 0.5\text{CH}_2\text{Cl}_2$: C, 65.12%; H, 4.45%; N, 7.50% (see Section 2). The ^1H nmr and ^{13}C nmr data are recorded in Table 3.

3.4. Crystal data

Crystals suitable for X-ray determination were obtained from chloroform solution. Data were collected on an automated Picker four-circle diffractometer using Ni-filtered CuK_α radiation with pulse height analysis. The diffractometer routine was that of Grant and Gabe

Table 1

Atom	$\delta(^1\text{H})$ ppm	Atom	$\delta(^1\text{H})$ ppm	Atom	$\delta(^1\text{H})$ ppm
H ₂ /H ₁₃	9.48	H ₁₆ /MH ₂₁	8.98	H ₂₈ /H ₃₃	7.53
H ₇ /H ₈	4.77	H ₁₈ /H ₁₉	8.29	H ₂₉ /H ₃₂	7.53
H ₁₅ /H ₂₂	8.48	H ₂₇ /H ₃₄	7.97	H ₃₀ /H ₃₁	7.29
Atom	$\delta(^{13}\text{C})$ ppm	Atom	$\delta(^{13}\text{C})$ ppm	Atom	$\delta(^{13}\text{C})$ ppm
C ₁ /C ₁₄	154.5	C ₁₅ /C ₂₂	127.6	C ₂₇ /C ₃₄	118.5
C ₂ /C ₁₃	158.2	C ₁₆ /C ₂₁	139.3	C ₂₈ /C ₂₉ /C ₃₂ /C ₃₃	116.3
C ₄ /C ₁₁	136.9	C ₁₇ /C ₂₀	130.1	C ₂₈ /C ₂₉ /C ₃₂ /C ₃₃	130.5
C ₅ /C ₁₀	152.7	C ₁₈ /C ₁₉	128.0	C ₃₀ /C ₃₁	122.7
C ₇ /C ₈	70.0	C ₂₄ /C ₂₅	145.7		

Table 2

Atom	$\delta(^1\text{H})$ ppm	Atom	$\delta(^1\text{H})$ ppm	Atom	$\delta(^1\text{H})$ ppm
H ₂ /H ₁₃	4.65	H ₁₆ /H ₂₁	8.49	H ₂₈ /H ₃₃	6.83
H ₇ /H ₈	4.38	H ₁₈ /H ₁₉	7.97	H ₂₉ /H ₃₂	6.83
H ₁₅ /H ₂₂	7.90	H ₂₇ /H ₃₄	6.91	H ₃₀ /H ₃₁	6.63
Atom	$\delta(^{13}\text{C})$ ppm	Atom	$\delta(^{13}\text{C})$ ppm	Atom	$\delta(^{13}\text{C})$ ppm
C ₁ /C ₁₄	158.1	C ₁₅ /C ₂₂	123.0	C ₂₇ /C ₃₄	109.6
C ₂ /C ₁₃	48.1	C ₁₆ /C ₂₁	136.8	C ₂₈ /C ₂₉ /C ₃₂ /C ₃₃	110.1
C ₄ /C ₁₁	137.3	C ₁₇ /C ₂₀	127.8	C ₂₈ /C ₂₉ /C ₃₂ /C ₃₃	121.0
C ₅ /C ₁₀	144.7	C ₁₈ /C ₁₉	126.1	C ₃₀ /C ₃₁	116.4
C ₇ /C ₈	70.0	C ₂₄ /C ₂₅	145.6		

Table 3

Atom	$\delta(^1\text{H})$ ppm	Atom	$\delta(^1\text{H})$ ppm	Atom	$\delta(^1\text{H})$ ppm
H ₂	6.56	H ₉ /H ₁₆	7.41	H _{28A} /H _{29A}	4.08
H ₃	4.50	H ₁₀ /H ₁₅	8.14	H _{28B} /H _{29B}	3.52
H ₄	4.39	H ₁₂ /H ₁₃	7.74	H _{29A} /H _{28A}	4.47
H ₅	4.60	H ₁₃ /H ₁₂	7.68	H _{29B} /H _{28B}	3.71
H _{2'}	4.80	H ₁₅ /H ₁₀	8.00		
H _{3'}	4.37	H ₁₆ /H ₉	7.13		
H _{4'}	4.25	H ₂₃ /H ₂₄			
H _{5'}	4.31	H ₂₅ /H ₂₆	multiplet		
H _{7A}	4.63	H ₃₁ /H ₃₂	6.74–7.37		
H _{7B}	5.89	H ₃₃ /H ₃₄			
H _{20A}	6.22				
H _{20B}	4.40				
Atom	$\delta(^{13}\text{C})$ ppm	Atom	$\delta(^{13}\text{C})$ ppm	Atom	$\delta(^{13}\text{C})$ ppm
C ₁ /C _{1'}	84.0	C ₈ /C ₁₇	155.1	C ₂₀	56.4
C ₂	72.6	C ₉ /C ₁₆	121.1	C ₇	58.0
C ₃	71.3	C ₁₀ /C ₁₅	135.8	C ₂₂ /C ₃₅	136.2
C ₄	70.7	C ₁₁ /C ₁₄	127.9	C ₂₃ /C ₂₄	130.5; 128.7
C ₅	72.6	C ₁₂ /C ₁₃	126.4	C ₂₅ /C ₂₆	128.5; 128.3
C _{1'} /C ₁	79.8	C ₁₃ /C ₁₂	125.6	C ₃₁ /C ₃₂	122.3; 121.5
C _{2'}	72.6	C ₁₄ /C ₁₁	127.7	C ₃₃ /C ₃₄	117.1; 114.9
C _{3'}	70.7	C ₁₅ /C ₁₀	135.9	C ₂₇ /C ₃₀	157.7
C _{4'}	72.0	C ₁₆ /C ₉	122.3	C ₂₈ /C ₂₉	68.8
C _{5'}	72.8	C ₁₇ /C ₈	154.7	C ₂₉ /C ₂₈	68.4
C ₆ /C ₂₁	172.1	C ₁₈ /C ₁₉	146.6	C ₃₀ /C ₂₇	155.9
C ₂₁ /C ₆	170.9	C ₁₉ /C ₁₈	146.2	C ₃₅ /C ₂₂	133.0

Table 4
Selected bond lengths and angles

(a) Bond lengths (Å)			
O ₁ /C ₆	1.224 (18)	N ₄ /C ₂₀	1.461
O ₂ /C ₂₉	1.436 (17)	N ₄ /C ₂₁	1.344
O ₂ /C ₃₀	1.357 (17)	N ₄ /C ₂₂	1.436
O ₃ /C ₂₇	1.378 (17)	C ₁ /C ₆	1.493
O ₃ /C ₂₈	1.422 (17)	C ₁ '/C ₂₁	1.493
O ₄ /C ₂₁	1.222 (18)	C ₇ /C ₈	1.501
N ₁ /C ₆	1.386	C ₁₇ /C ₂₀	1.511
N ₁ /C ₇	1.470		
N ₁ /C ₃₅	1.394		

(b) Bond angles (°)			
C ₆ -N ₁ -C ₇	116.1	O ₄ -C ₂₁ -N ₄	122.3
C ₆ -N ₁ -C ₃₅	124.9	O ₄ -C ₂₁ -C ₁ '	119.4
C ₇ -N ₁ -C ₃₅	116.0	C ₁ '-C ₂₁ -N ₄	118.3
C ₂₀ -N ₄ -C ₂₁	126.4	O ₃ -C ₂₈ -C ₂₉	110.4
C ₂₀ -N ₄ -C ₂₂	116.4	O ₂ -C ₂₉ -C ₂₈	108.4
C ₂₁ -N ₄ -C ₂₂	117.0	O ₂ -C ₃₀ -C ₃₁	123.4
O ₁ -C ₆ -N ₁	122.2		
O ₁ -C ₆ -C ₁	120.2		
C ₁ -C ₆ -N ₁	117.6		

[21]. Crystal data are: monoclinic, P2₁c, $a = 11.428(11)$, $b = 27.927(12)$, $c = 10.904(7)$ Å; $\beta = 107.26(07)^\circ$; $Z = 4$ molecules per cell. Structure analysis was by direct methods using SOLVER (NRCVAX) [22]. Full matrix anisotropic refinement by least squares was uneventful. Fig. 2 shows the structure of the molecule and Table 4 shows selected bond lengths and bond angles. Fractional atomic coordinates have been deposited with the Cambridge Organic Structure Database.

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