Synthesis and characterisation of some novel β-aminodiketones

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Abstract. The synthesis and characterisation of five new β-aminodiketones is reported: (a) 3,3,5,8,10,10-hexamethyl-5,8-diazadodecane-2,11-dione; (b) 3,3,11,11-tetramethyl-5,8-diazatridecane-2,12-dione; (c) 3,3,12,12-tetramethyl-5,10-diazatetradecane-2,13-dione; (d) 3,3,10,10-tetramethyl-5,8-diphenyl-5,8-diazadodecane-2,11,dione and (e) 6,7-benzo-3,3,10,10-tetramethyl-5,8-diazadodecane-2,11-dione. These compounds are discussed as potential precursors in the synthesis of tetra-aza macrocyclic complexes.

Keywords. β-aminodiketone; tetra-aza macrocyclic complexes; nuclear magnetic resonance; mass spectra.

1. Introduction

The synthesis of β-aminodiketones is of interest since these compounds are possible precursors in the synthesis of model systems of naturally occurring tetra-aza macrocyclic systems such as the corrinoids and porphyrins. A variety of β-aminodiketones have been synthesised which have resulted in the preparation of a wide variety of tetra-aza macrocyclic complexes exhibiting variation in ring size, ring substitution and degree of saturation within the ring system. The synthesis of such model systems is achieved by one of two general procedures—a metal template synthesis as described by Curtis and House (1961) and Busch and Blinn (1968) or by metal insertion into a pre-formed tetra-aza macrocyclic ligand, formed by condensation of an aminodiketone with a primary amine. Love and Powell (1968) synthesised 4,4,9,9-tetramethyl-5,8-diazadodecane-2,11-dione [1], Green and Tasker (1968) synthesised 4,7-diaza-2,3,8,9-dibenzodecane-1,10-dione [2] and Bishop *et al* (1978) synthesised 1,10-phenanthroline-2,9-dicarboxaldehyde [3], all of which have served as precursors for a variety of Ni(II) tetra-aza macrocyclic complexes formed *via* a metal template synthesis. The α-aminodiketone [3] is an interesting example of the requirement of a dicarbonyl compound in general to contain one or more donor atoms between two carbonyl groups to achieve a facile *in situ* metal directed condensation, as discussed by Lindoy and Busch (1971). Further examples of synthetic β-aminodiketones include *bis*(acetylacetone)ethylenediamine [4], Martell *et al* (1955), N,N'-*bis*(2-acetyl-2-methylpropyl)piperazine [5], Lesnewski (1978) and 3,3,10,10-tetramethyl-5,8-diazadodecane-2,11-dione [6], Roe *et al* (1982). Compounds [5] and [6] were prepared by condensing appropriate diaminedihydrochloride with formaldehyde and methylisopropyl ketone, according to the Mannich reaction scheme.

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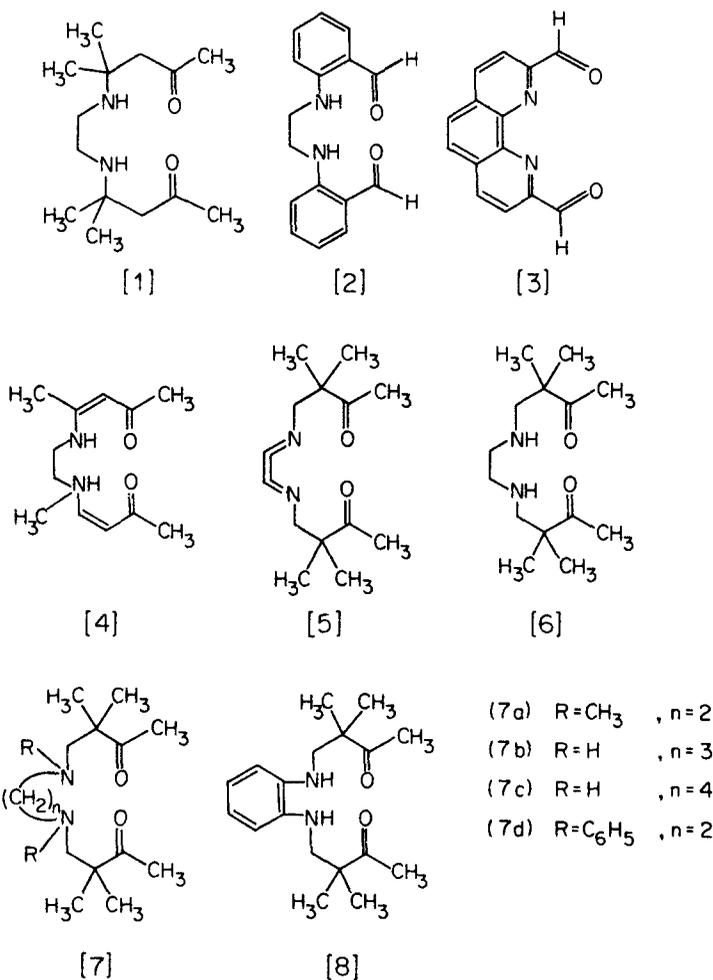
In the present study, five new β-aminodiketones [7 a–d], [8], structurally related to [1], [5] and [6] are synthesised and characterised from corresponding infrared, proton NMR, electronic and mass spectral data.

2. Experimental

All chemicals used were of reagent grade. Elemental analyses were provided by the Australian Microanalytical Service, Melbourne.

β-aminodiketones were prepared according to the procedure described by Roe *et al* (1982) for compound [6] or a modification thereof.

IR spectra in the range 4000–250 cm^{-1} were obtained on a Perkin-Elmer 457 spectrophotometer using the NaCl disc method.

Proton NMR spectra were obtained on a Perkin-Elmer R32 high resolution nuclear magnetic resonance spectrometer using Me$_4$Si as an internal reference and a sample spinning rate of 30 Hz.

Electron impact and chemi-ionisation mass spectra were obtained using a JEOL-JMSD 100 mass spectrometer and an ionising voltage of 70 eV with isobutane as carrier gas for the chemi-ionisation mode. Boiling points were obtained using a Swoloboff apparatus as described by Vogel (1972). It is apparent that these β-aminodiketones form azeotropes with either water or ether. Electronic spectra were recorded on a Shimadzu UV-240 recording spectrophotometer using 1 cm quartz cells and acetonitrile-190 as solvent.

2.1 3,3,5,8,10,10-*hexamethyl-5,8-diazadodecane-2,11-dione* [7a]

Using the general procedure described by Roe *et al* (1982), N,N'-dimethylethylene-diamine dihydrochloride (12·0 g); methyl isopropyl ketone (12·0 g); formaldehyde (37% w/v, 11·7 cm³) were refluxed to yield 5·0 g (42·2%) of a red oil b.p. 135°. i.r. v_{max}(cm⁻¹): 3400 sb (O–H str, H_2O), 2950 s, 2830 s, (C–H str, N–CH_3), 2965 s, 2870 s, (C–H str, CH_3), 2800 s (C–H str, CH_2), 1705 vs (C=O str), 1465 s, (C–H def, CH_2 scissor), 1380 s, 1355 s, (C–H def, gem–Me), 1260 s, 1185 s, 1110 s, 1035 s, (C–N str), 955 m, 835 m (C–C str).

^{1}H-NMR (CDCl₃): 1·17, s, 12H, gem–Me; 2·15, s, 6H, N-Me; 2·20, s, 6H, MeC=O; 2·50, d, 4H, CH_2; 2·62, s, 4H, CH_2 Mass Spectrum (c.i.) m/z 285 (molecular ion), 142 ($CH_2N(Me)CH_2C(Me)_2COMe$), 100($H_2CNH \cdot CH_2CH_2NMe \cdot CH_2$), 86 ($CH(Me)_2COMe$), 71($CH(Me)_2CHO$), 58($HNCH_2CH_2NH$), 43(MeCO), 28 ($CH_2CH_2$).

Microanalysis. (Found: C, 66·6, H, 11·20; N, 9·85. $C_{16}H_{32}N_2O_2$, 0·25 H_2O requires C, 66·51; H, 11·33; N, 9·7%).

2.2 3,3,11,11-*tetramethyl-5,8-diazatridecane-2,12-dione* [7b]

Using the general procedure, 1,3-diaminopropane dihydrochloride (13·2 g), methyl-isopropyl ketone (21·4 g), formaldehyde (37% w/v, 19·39 cm³) were refluxed to yield 13·14 g (41%) of a red oil. b.p. 91°. i.r. v_{max}(cm⁻¹): 3400 sb (O–H) str, H_2O), 3330 s, (N–H str), 2960 s, 2870 s, (C–H str, CH_3), 2930 s, 2820 s, (C–H str, CH_2), 1705 vs (C=O str with shoulder at 1645 m), 1590 m (N–H def), 1465 s (C–H def, CH_2 scissor), 1380 m, 1355 s, (C–H def, gem–Me), 1265 m, 1190 m, (C–N str), 1050 m, 965 m, 950 mb, 880 m (C–C str). Strong bands at 1120 s, 1100 s imply a C–O str vibration. ^{1}H-NMR (d₆-DMSO): 1·1, s, 12H, gem–Me; 2·2, m, 6H, MeC=O; 3·2, s, 2H, NH; 4·57; s, 2H, H_2O. Chemical shifts at 3·7, 3·62, 3·54, 3·47, q, and 1·2, 1·12, 0·97, *t* indicate the presence of ether resulting from the extraction procedure. It is apparent that decomposition of the diketone occurs prior to complete removal of ether. Mass spectrum (c.i.): m/z 270 (molecular ion), 86 ($HC(Me)_2COMe$), 84 ($CH_2C(Me)_2CO$), 43(MeCO), 28 (CH_2CH_2). Fragments at m/z 74 and 45 correspond to ether fragments ($MeCH_2OCH_2Me$) and (OCH_2Me) respectively.

Microanalysis: (Found: C, 58·12; H, 11·32; N, 7·63. $C_{15}H_{30}N_2O_2$, 2·5 H_2O requires C, 58·57; H, 11·64; N, 7·19%).

2.3 3,3,12,12-*tetramethyl-5,10-diazatetradecane-2,13-dione* [7c]

Using the general procedure with a revised stoichiometry 1 mol of diamine dihydro-chloride, 5 mol methylisopropyl ketone, 2·5 mol formaldehyde, 0·2 cm³ hydrochloric acid (32% w/w) in anhydrous methanol (200 cm³) were refluxed at 68° under N_2 for

12 hr, the reactants of 1,4-diaminobutane dihydrochloride (10·6 g), methyl isopropyl ketone (28·4 g) and formaldehyde (37% w/v, 13·4 cm^3) produced a yellow oil of yield 6·5 g (34·5%), b.p. 76°. IR v_{max} (cm^{-1}): 3375sb (N–H str), 2942s, 2910s (C–H str, CH$_2$), 1690s (C=O str), 1455s (C–H def, CH$_2$ scissor), 1375m, 1350s, (C–H def, gem-Me), 1185w, 1120s (C–N str). ^{1}H-NMR (d$_6$-DMSO): 1·08, s, 12H, gem-Me; 1·98, s, 6H, MeC=O, 3·03, s, 12H, CH$_2$. Mass spectrum (c.i.): m/z 142 (MeCOC(Me)$_2$CH$_2$NHCH$_2$CH$_2$), 86 (MeCOC(Me)$_2$H), 57 (CH$_2$NHCH$_2$CH$_2$), 43 (MeCO), 42 (Me$_2$C). Microanalysis: (Found: C, 67·56; H, 11·34; N, 9·84; C$_{16}$H$_{32}$N$_2$O$_2$, 0·25 C$_4$H$_{10}$O requires C, 67·39; H, 11·47; 9·24%).

2.4 3,3,10,10-*tetramethyl*-5,8-*diphenyl*-5,8-*diazadodecane*-2,11-*dione* [7d]

Using the revised procedure as for [7c], N,N'-diphenylethylenediamine dihydrochloride (7·0 g), methyl isopropyl ketone (10·6 g), formaldehyde (37% w/v, 5·0 cm^3) were refluxed to produce a red-oil of yield 3·6 g (36%). b.p. 151°. i.r. v_{max} (cm^{-1}): 3070m, 3040s, 3000s (C–H str on C$_6$H$_5$), 3340s, (O–H str, H$_2$O), 2950s, 2850s (C–H str, CH$_3$), 2920s (C–H str, CH$_2$), 1695s (C=O str), 1660s, 1590s, 1495sb, 1430m (C=C str of C$_6$H$_5$), 1460m (C–H def, CH$_2$ scissor), 1375m, 1350s (C–H def, gem–Me), 1300m, 1290m, 1255s, 1215s, 1185m, 1150m (C–N str), 1110s, 1090m, 1070m, 1025m, 975s, 880s, 830m, 800m (C–C str), 750s, 690s (C–H def, monosubstituted aromatic, C$_6$H$_5$, out of plane).

^{1}H-NMR (d$_6$-DMSO): 1·11, 1·13, d, 12H, gem-Me, 2·13, s, 6H, CH$_3$C=O, 4·52, s, 4H, CH$_2$, 4·58, s, 4H, CH$_2$ on *en* bridge, 6·83 sextuplet, J = 7 Hz, ϕ, 7·43, s, 12H, CH ϕ. Mass Spectrum (e.i.) m/z: 238(CH$_2$N(C$_6$H$_5$)CH$_2$CH$_2$N(C$_6$H$_5$)CH$_2$), 133 (CH$_2$N(C$_6$H$_5$)CH$_2$CH$_2$), 119 (CH$_2$N(C$_6$H$_5$)CH$_2$), 86 ((Me)$_2$CCOMe), 43 (MeCO), 42 (Me$_2$C).
Microanalysis: (Found: C, 74·53; H, 8·67; N, 9·07. C$_{26}$H$_{36}$N$_2$O$_2$ 0·5 H$_2$O requires C, 74·78; H, 8·93; N, 6·70%).

2.5   6,7-*benzo*-3,3,10,10-*tetramethyl*-5,8-*diazadodecane*-2,11-*dione* [8]

Using the revised procedure as for [7c], o-phenylenediamine dihydrochloride (10·0 g), methyl isopropyl ketone (26·7 g), formaldehyde (37% w/v, 11·2 cm^3) were refluxed to produce a red-oil of yield 14·0 g (84%). b.p. 130°. IR v_{max} (cm^{-1}): 3400sb (N–H str), 3040m (C–H str, C$_6$H$_4$), 2950s, 2910s (C–H str, CH$_3$), 2850s, (C–H str, CH$_2$), 1695s (C=O str), 1675s, 1590s, 1490w, 1450wb (C=C str on C$_6$H$_4$), 1505w (N–H def), 1380w, 1350w, (C–H def, gem–Me), 1030m, 1095m (C–N str), 735s (C–H def out of plane disubstituted aromatic, C$_6$H$_4$).

^{1}H-NMR (d$_6$-DMSO): 1·1, s, 12H, gem–Me; 2·07, s, 6H, MeC=O; 3·19, s, 2H, NH; 7·1, q, 4H, ϕ. Mass spectrum (e.i.): m/z 261 (Me$_2$CCH$_2$NH(C$_6$H$_4$)NHCH$_2$C(Me)$_2$COMe) 219 (CH$_2$NH(C$_6$H$_4$)NHCH$_2$C(Me)$_2$COMe), 86 (Me$_2$CCOMe) 73 (Me$_2$CHCH$_2$NH$_2$), 71 (Me$_2$CHCO), 43 (MeCO), 42 (Me$_2$C).
Microanalysis: (Found: C, 64·68; H, 9·52; N, 10·09. C$_{18}$H$_{28}$N$_2$O$_2$ · 1·5H$_2$O requires C, 65·22; H, 8·97; N, 8·45%).

3. Results and Discussion

3.1 $^1H_{NMR}$ *Spectral assignments*

With respect to structure [7a], the singlet at 1·11 δ is assigned to the geminal dimethyl

[9]   [10]   [11]
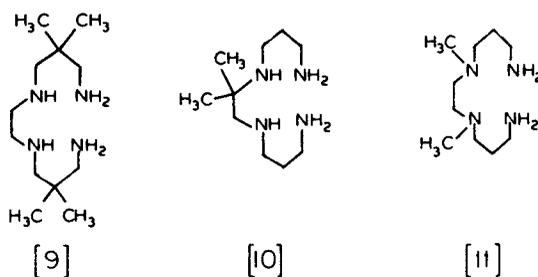
groups; the singlet at 2·5 δ is assigned to the N–Me function and singlet at 2·2 δ is assigned to the MeC=O function. These assignments for the geminal dimethyl groups and the N–Me function are in accordance with the assignments of Barefield *et al* (1976) for structures [9], [10] and [11]: (gem–Me, 0·86 δ [9], 1·0 δ [10] and N–Me 2·18 δ, [11]). For structure [7b], the singlet at 3·2 δ is assigned to the N–H group, which is in contrast to the singlet at 1·5 δ for structure [10] and [11] as assigned to N–H by Barefield *et al* (1976). The assignments for the geminal dimethyl groups and for the MeC=O function are also in agreement with the corresponding assignments 1·1 and 2·14 δ respectively made by Lesnewski (1978) for structure [5].

For structure, [7c], [7d] and [8], the chemical shifts corresponding to the MeC=O function are moved upfield by 0·22, 0·07 and 0·13 δ respectively, reflecting expansion and contraction of the carbon chain length between the amine functions. Structure [7d] exhibits a doublet at 1·11 and 1·13 δ for the geminal-methyl groups, possibly due to an anisotropic effect, that is, the geminal-methyl groups resonate at different chemical shift positions due to shielding of one methyl group relative to the double bond of the MeC=O function.

3.2 IR *spectral assignments*

IR assignments for the β-aminodiketones synthesised in the present work are made on the basis of the definitive group assignments provided by Kemp (1975), Jones (1959) and Silverstein *et al* (1974).

The most characteristic band for these compounds is that due to the C=O stretching vibration in the region of 1700 cm^{-1}. All five compounds indicate such a band within the narrow range 1700 ± 5 cm^{-1} which is indicative of a similar environment for carbonyl groups within the series.

Further characteristic bands for aminodiketones according to Kemp (1975) and Jones (1959) are those associated with C–H deformation modes of geminal methyl groups in the region of 1390 and 1360 cm^{-1} respectively. For the five β-aminodiketones studied, these bands appear at 1380 ± 5 cm^{-1} and 1350–1355 cm^{-1}. Compounds [7a], [7b] and [7c], which have a $(CH_2)_n$ bridge between secondary or tertiary amine groups, exhibit a CH_2 scissor vibration at 1460 ± 5 cm^{-1}.

Compounds [7b], [7c] and [8] exhibit an N–H stretching vibration at 3330, 3375 and 3400 cm^{-1} respectively.

The phenyl groups attached to the tertiary nitrogen atoms in compound [7d] are identified by the following bands: C–H stretching vibrations at 3070 cm^{-1} (s), 3040 cm^{-1} (s) and 3000 cm^{-1} (s), C=C stretching vibrations at 1660 cm^{-1} (s), 1590 cm^{-1} (s), 1495 cm^{-1} (sb) and 1430 cm^{-1} (m). The main fingerprint bands are the

C–H deformation out-of-plane bands at $750 \, \text{cm}^{-1}$ (s) and $690 \, \text{cm}^{-1}$ (s), typical of mono-substituted aromatic compounds. The *o*-phenylene group in compound [8] is identified by C=C stretching vibrations at $1675 \, \text{cm}^{-1}$ (s), $1590 \, \text{cm}^{-1}$ (s), $1490 \, \text{cm}^{-1}$ (w) and $1450 \, \text{cm}^{-1}$ (wb), with the main fingerprint band at $735 \, \text{cm}^{-1}$ (s) corresponding to the C–H deformation out-of-plane mode for a di-substituted aromatic compound.

IR spectra over the range $1800–1300 \, \text{cm}^{-1}$ for compounds [6], [7b] and [7d] indicating C=O str., C–H def. CH_2 str. and C–H def (gem–Me) bands are shown in figure 1.

3.3 *Mass spectral assignments*

In general, mass spectra derived *via* the chemi-ionisation mode indicate molecular ions whereas mass spectra derived *via* the electron impact mode show fragment ions only.

All five β-aminodiketones exhibit α cleavage—a common fragmentation pathway according to McLafferty (1973). Such cleavage occurs between pairs of carbon atoms C_1–C_2, C_1–C_2', C_2–C_3, C_2'–C_3' [12] resulting in common fragment ions of m/z 86 $(CH(Me)_2COMe, 43 (COMe)$ and 42 (CMe_2).

Further α type cleavage occurs for compounds [7a] and [7c] within the ethylenedi-amine and 1,3-diaminobutane bridges respectively, yielding fragment ions of m/z 142 $(CH_2N(Me)CH_2C(Me)_2COMe)$ [7a] and 142 $(MeCOC(Me)_2CH_2NH$ $CH_2 \cdot CH_2)$ [7c]. Compound [7d] gave a fragment ion at m/z 119 $(CH_2N(C_6H_5)CH_2)$, however such cleavage within the ethylenediamine bridge is secondary to the α cleavage
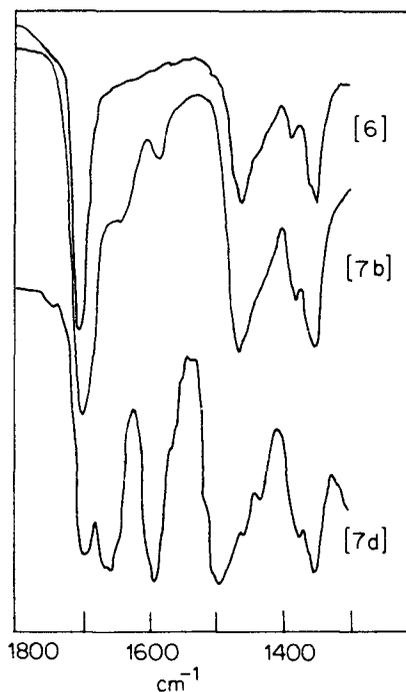
Figure 1. IR spectra of compounds [6], [7b] and [7d] in the region of $1800 \, \text{cm}^{-1}$ to $1300 \, \text{cm}^{-1}$.

[12]
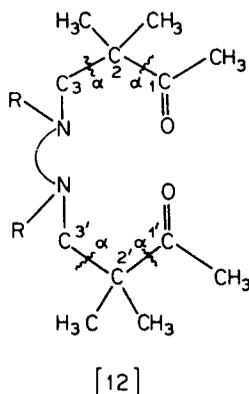
between C_1–C_2 and C_2–C_3 type segments since a fragment ion corresponding to $(CH_2N(C_6H_5)CH_2C(Me)_2COMe)$ does not appear in the mass spectrum of this compound.

3.4 *Electronic spectral assignments*

The principal uv-visible spectral bands within the range 190–900 nm for various β-aminodiketones are listed in table 1.

The assignment of bands is made on the basis of the definitive data of Silverstein *et al* (1974); a band in the region of 280 nm, $\varepsilon_{max} = 15$ is assigned to the $n \to \pi^*$ forbidden transition in the carbonyl chromophore. Methylisopropyl ketone, the precursor of the β-aminodiketones studied, indicates an electronic absorption band at 280 nm, $\varepsilon_{max} = 23\cdot5$ (acetonitrile solvent). The $n \to \sigma^*$ and $\pi \to \pi^*$ allowed transitions for such ketones are of higher energy $n \to \sigma^*$ (185 nm) and $\pi \to \pi^*$ (160 nm) and are outside the scanning range studied. All β-aminodiketones studied exhibit the $n \to \pi^*$ forbidden transition, which is essentially the fingerprint transition for these compounds.

The additional bands associated with compound [8] are assigned to the $\pi \to \pi^*$ transitions of the C_6H_4 moiety: 283 nm $(A_{1g} \to B_{2u})$, 275 nm $(A_{1g} \to B_{1u})$ and 248 nm $(A_{1g} \to E_{1u})$, as compared to those of benzene at 204 nm $(A_{1g} \to B_{1u})$ 256 nm $(A_{1g} \to B_{2u})$ and 184 nm $(A_{1g} \to E_{1u})$. The substantial bathochromic shift accompanied by a diminished fine structure is due to the non-bonding pair substituents of NH_2. The fine structure is lost due to $n-\pi$ conjugation and the shift is due to conjugation between the

Table 1. Electronic spectra of β-aminodiketones (acetonitrile solvent).

| Compound | λ_{max} (nm) $(\varepsilon_{max})(10^{-2} \ M^2 \ mol^{-1})$ | | | |
	$n \to \pi^*$	$A_{1g} \to B_{2u}$	$A_{1g} \to B_{1u}$	$A_{1g} \to E_{1u}$
[7b]	312 (1317)	—	—	—
[7c]	292 (38)	—	—	—
[7d]	379 (252·5)	—	—	—
[8]	304 (2475)	283 (3197)	275 (3919)	248 (7529)
[6]	297·5 (70·3)	—	—	—
[5]	279 (366)			

non-bonding electrons of nitrogen and the π-electron system of the ring.

It is interesting that only one band is observed for compound [7d] at $\lambda_{max} = 379$ nm ($\varepsilon_{max} = 252 \cdot 5$) which probably results from the overlap of a shifted $n \rightarrow \pi^*$ forbidden transition in the carbonyl chromophore and a shifted $A_{1g} \rightarrow B_{2u}$ allowed transition associated with the aromatic substituents on the nitrogen atoms.

4. Conclusion

The physical data for the five β-aminodiketones synthesised in the present work are essentially consistent with their proposed structures. Such compounds increase the range of known aminodiketones, in particular, those reported by Martin *et al* (1980), Busch and Blinn (1968) Martell *et al* (1955), Holm *et al* (1973), Lesnewski (1978), Roe *et al* (1982), Barefield *et al* (1976), Martell *et al* (1958), Belford *et al* (1956), Jager (1964, 1968), Truex and Holm (1972), Tasker and Fleischer (1970), Van Leeuwen (1968), Nakamura and Kawaguchi (1968), Bamfield (1969), Patterson and Holm (1975), and Black *et al* (1972) which have been employed in the synthesis of a wide variety of tetra-aza macrocyclic complexes.

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