

# $^{17}\text{O}$ NMR studies on $\alpha$ -diamides

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Received 4 August 1997; revised 21 October 1997; accepted 21 October 1997

**ABSTRACT:**  $^{17}\text{O}$  NMR spectra of several  $\alpha$ -diamides were obtained at natural isotopic abundance in acetonitrile solution in order to study the conformations of these compounds in solution. The  $^{17}\text{O}$  NMR shifts vary with the intercarbonyl dihedral angle  $\alpha$  in a sense opposite to that observed for  $\alpha$ -diketones. © 1998 John Wiley & Sons, Ltd.

**KEYWORDS:**  $\alpha$ -diamides;  $^{17}\text{O}$  NMR; conformation

## INTRODUCTION

The carbonyl group is one of the main functional groups in organic chemistry and it has been widely studied by numerous methods, including the  $^{17}\text{O}$  NMR technique.<sup>1</sup> The nature of the bond and the preferred orientation of this group with respect to other groups in its neighborhood are strongly influenced by interactions with vicinal substituents and both aspects have been investigated.<sup>2,3</sup> The amino group is most important among possible vicinal substituents, and amides have been the subject of a large body of  $^{17}\text{O}$  NMR work.<sup>4</sup> However, whereas the particular but important case of  $\alpha$ -diketones has already been dealt with, at least partially<sup>2c,3a–d</sup> the only paper on  $\alpha$ -diamides is a report on the shifts of  $N,N'$ -dimethyl- and  $N,N'$ -diphenyloxamides (291.9 and 313.2 ppm, respectively, in DMSO at 90°C), in a study devoted to related quinoxaline-2(1*H*),3(4*H*)-diones.<sup>5</sup>

The recent availability of  $N,N'$ -disubstituted-4,5-imidazolidinediones<sup>6</sup> offers the opportunity to study  $\alpha$ -diamides in a fixed planar *cis* configuration.<sup>6a</sup> Following our studies on  $\alpha$ -diketones,<sup>2c,3d</sup> it was also of interest to compare these closely related systems.

## RESULTS AND DISCUSSION

Scheme 1 shows the structural formulae of the compounds studied. Values of the intercarbonyl dihedral angles of several  $\alpha$ -diamides obtained in different ways are given in Table 1, which also gives  $^{17}\text{O}$  NMR chemical shifts and estimated half-height linewidths in acetonitrile solution.

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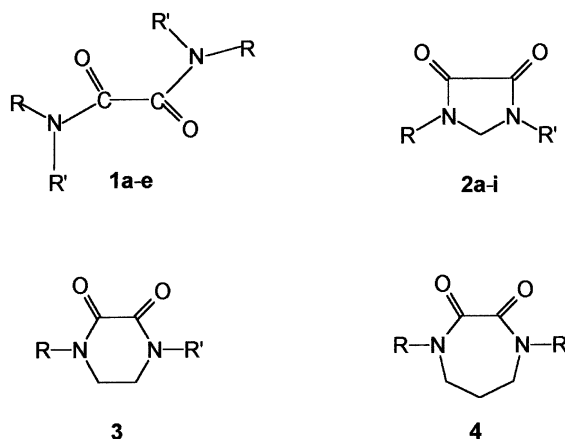
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As a general remark, we can note that  $^{17}\text{O}$  NMR shifts of the studied  $\alpha$ -diamides fall in the range (ca. 270–370 ppm) of common amides.<sup>7a</sup> Several effects cooperate in influencing the observed chemical shifts. In our attempt to estimate the effects of individual factors on the chemical shifts, we compared homogeneous subgroups of compounds.

Substitution on the amide nitrogen strongly influence the  $^{17}\text{O}$  NMR shifts of the conjugated carbonyl group. On going from **2a,b** to **2c–i** a deshielding of roughly 25 ppm is observed, which can be attributed to the influence of the aromatic ring and its substituents as previously reported for simple amides.<sup>7a,b</sup>

The changes in shifts induced by substitution in the aryl ring for the group of the anilides **2c–i** are comparable to those observed<sup>7b</sup> for acetanilides,  $\Delta\delta(\mathbf{2c} - \mathbf{2h}) = 1.9$  ppm and  $\Delta\delta(\mathbf{2c} - \mathbf{2i}) = -4.1$  ppm vs 3.3 and  $-3.7$  ppm for 4-methyl and 4-chlorophenylacetanilides, respectively. In the case of *ortho*-substitution, **2d** compared with **2f**, steric hindrance causes shielding, opposite to the usual effect in  $^{17}\text{O}$  NMR spectroscopy,<sup>8</sup>



Scheme 1.

**Table 1.**  $^{17}\text{O}$  NMR data on  $\alpha$ -diamides in MeCN solution at 65 °C

Compound	R	R'	$\delta\text{O-17}$ (ppm)	$\nu_{\frac{1}{2}}$ (Hz)	$\theta$ (°)
<b>1a</b> <sup>a</sup>	H	H	306.2	270	180 <sup>19</sup>
<b>1b</b>	<sup>i</sup> Pr	<sup>i</sup> Pr	317.6	340	92 <sup>13</sup>
<b>1c</b>	H	<sup>t</sup> Bu	294.7	222	180 <sup>b</sup>
<b>1d</b>	H	1-Ad	292.4	410	180 <sup>b</sup>
<b>1e</b> <sup>c</sup>	Me	C <sub>6</sub> H <sub>5</sub>	336.5, 349.1	295, 320	135 <sup>b</sup>
<b>2a</b>	Me	Me	285.5	105	0 <sup>b</sup>
<b>2b</b>	C <sub>6</sub> H <sub>11</sub>	C <sub>6</sub> H <sub>11</sub>	285.7	375	0 <sup>b</sup>
<b>2c</b>	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	313.0	280	0 <sup>6a</sup>
<b>2d</b>	<i>o</i> -FC <sub>6</sub> H <sub>4</sub>	<i>o</i> -FC <sub>6</sub> H <sub>4</sub>	307.1	320	0 <sup>b</sup>
<b>2e</b>	<i>m</i> -FC <sub>6</sub> H <sub>4</sub>	<i>m</i> -FC <sub>6</sub> H <sub>4</sub>	319.1	270	0 <sup>b</sup>
<b>2f</b>	<i>p</i> -FC <sub>6</sub> H <sub>4</sub>	<i>p</i> -FC <sub>6</sub> H <sub>4</sub>	311.2	275	0 <sup>b</sup>
<b>2g</b>	<i>m</i> -MeC <sub>6</sub> H <sub>4</sub>	<i>m</i> -MeC <sub>6</sub> H <sub>4</sub>	310.4	250	0 <sup>b</sup>
<b>2h</b>	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	311.1	385	0 <sup>b</sup>
<b>2i</b>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	317.1	360	0 <sup>b</sup>
<b>3</b>	Me	Me	323.0	135	18 <sup>d</sup>
<b>4</b>	Me	Me	325.3	134	78 <sup>d</sup>

<sup>a</sup> Measured in DMSO at 65 °C.

<sup>b</sup> Estimated, this work.

<sup>c</sup> Two signals for the two conformers were observed; see text.

<sup>d</sup> Computed by the semi-empirical quantum mechanical method AM1.<sup>23</sup>

but similar to the effect observed for the acetanilides.<sup>7b</sup> The influence of *meta* substitution is also consistent with previous observations. Compound **2e** is deshielded by 6.1 ppm compared with **2c**, a value close to those of 6.2 and 5 ppm measured for *meta*-substituted  $\alpha,\alpha,\alpha$ -trifluoroacetophenones<sup>9</sup> and anisoles,<sup>10</sup> respectively. The influence of a *meta*-methyl group, a shielding of 2.6 ppm, is opposite and weaker, as also noted, e.g., for acetophenones<sup>11</sup> (2 ppm) and  $\alpha,\alpha,\alpha$ -trifluoroacetophenones<sup>9</sup> (3.2 ppm).

These findings are in agreement with the results obtained, for the solid state,<sup>6a</sup> in the case of **2c**. For this compound, the aryl rings were found to be almost coplanar to the heterocyclic plane (torsional angle  $\approx 20^\circ$ ). Moreover, in acetanilide, a very similar ( $21^\circ$ ) torsional angle between the phenyl ring and the C=O group has been calculated,<sup>7b</sup> and also measured ( $17.6^\circ$ ) by x-ray crystallography.<sup>12</sup> We can therefore say that there are no important conformational changes for derivatives **2** on going from the solid state to solution.

The very close similarity of the shifts shown by **2a** and **2b** indicates that the N-substituent does not exercise steric hindrance on the carbonyl oxygen.

One of the most studied feature of  $\alpha$ -diketones is their intercarbonyl dihedral angle  $\theta$ . Its changes modify, *inter alia*, the electron density on the oxygen atoms,<sup>3a</sup> thus causing relevant effects on their  $^{17}\text{O}$  NMR chemical shifts. Cerfontain *et al.*<sup>3a</sup> determined, for the  $^{17}\text{O}$  NMR signals, a shift to higher field on increasing  $\theta$  from 0 to  $90^\circ$  and an opposite shift to lower field on further increasing  $\theta$  from  $90$  to  $180^\circ$ .

Also in the case of  $\alpha$ -diamides, the data in Table 1 show a dependence of the  $^{17}\text{O}$  NMR shifts on the angle  $\theta$ . It is worth noting, however, that this dependence is opposite to that observed for  $\alpha$ -diketones. In fact, **1b**

( $\theta = 92^\circ$ )<sup>13</sup> is deshielded by 32.1 ppm compared with **2a**. Such a value of the torsional angle  $\theta$  of **1b** had been hypothesized, in solution, based on dynamic NMR measurements,<sup>13a</sup> and has been measured, in the solid state, by x-ray analysis.<sup>13b</sup>

The observed deshielding can be assigned only to a minor extent to the influence of the isopropyl groups. We have previously pointed out that, on going from **2a** to **2b**, neither any observable steric effect nor any influence due to different electron release abilities of the two different alkyl groups could be ascertained. This observation is not uncommon in  $^{17}\text{O}$  NMR. *N,N*-dimethyl- and *N,N*-diethylacetamides<sup>14,15</sup> differ in their chemical shifts by only one ppm. Likewise, *N,N*-dimethyl- and *N,N*-diisopropyl-*N*-nitrosamines<sup>16</sup> show a 2 ppm difference. A possible buttressing effect from the isopropyl groups has been relieved by the change in the intercarbonyl dihedral angle (this is commonly assumed to be the reason for this effect). In any case, such an effect would have been opposite, i.e. shielding, as discussed previously.

Recently, Yamada<sup>17</sup> has shown that a change of the C(O)—N twist angle has a strong influence on the  $^{17}\text{O}$  NMR shifts of amides, i.e. as the twist angle  $\tau$  increases from about  $20^\circ$  towards  $90^\circ$ , deshielding is observed. This finding seems, however, not to be applicable to the observed deshielding of **1b** compared with **2a**. In fact, both compounds have a  $\tau$  value close to  $0^\circ$ , **2a** because of its geometrical constraints whereas **1b** is known,<sup>13b</sup> from an x-ray study, to have such a  $\tau$  value.

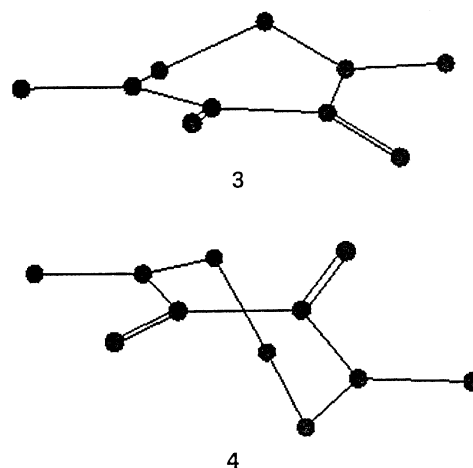
A possible contribution to the observed deshielding could come from cyclization. As observed by Boykin *et al.*,<sup>18</sup> it is problematic to find a monotonic relationship between chemical shifts and ring size in lactams for both  $^{17}\text{O}$  and  $^{15}\text{N}$  NMR. Comparison of five-membered ring C- or *N*-alkyl-substituted lactams ( $\Delta\delta = 6.6$  ppm),<sup>18</sup> with

similar open-chain amides<sup>4</sup> indicates that cyclization (to a five-membered ring) causes in the amide system a small contribution both upfield and downfield, depending on the derivatives compared. Even taking in account the differences between amides and  $\alpha$ -diamides, it seems reasonable not to ascribe to cyclization the full observed variation in chemical shifts between **1b** and **2a**.

A comparison between open-chain  $\alpha$ -diamides with  $\theta = 180^\circ$  (**1a**) and **1b** can be helpful. Compound **1a** is known to exist in such a conformation in the solid state.<sup>19</sup> The estimated<sup>20</sup> torsional angle  $\theta$  for *N,N'*-dialkyl-substituted  $\alpha$ -diamides in solution is roughly the same. Similar results are obtained by MMX calculations, as implemented in the program PC Model,<sup>21</sup> for derivatives **1c** and **1d**. The observed  $\Delta\delta(\mathbf{1b-1c})$  is 22.9 ppm. This observation is in good agreement with the previously discussed effect of  $\theta$  variation for derivatives **1b** and **2a**. That a difference in  $\Delta\delta$  is observed on comparing a  $\theta$  variation from  $0^\circ$  to  $90^\circ$  with that from  $90^\circ$  to  $180^\circ$  is not surprising. A similar result had been obtained in the case of  $\alpha$ -diketones.<sup>3a</sup> The small deshielding observed on comparing **1c** (and **1d**) with **2a** (*ca* 10 ppm) therefore has to be shared between this effect and that (if any) of cyclization. Compound **1a** has been measured, because of its very low solubility, in a solvent (DMSO) different from that (MeCN) of all the other derivatives. Contributions to its shift from hydrogen bonding are therefore different and it lacks *N*-alkyl groups; all this makes it difficult to quantify the influence of  $\theta$  variations. Its shift is, however, in qualitative agreement with the results discussed previously.

Compounds **3** and **4** are deshielded by 37.5 and 39.8 ppm, respectively, when compared with **2a**. These data are intriguing, as the torsional angle  $\theta$  is very different for the two compounds. These values have been reported<sup>22</sup> to be  $20^\circ$  and  $60^\circ$  for **3** and **4**, respectively. We newly computed them by the semi-empirical quantum mechanical method AM1, implemented in the Spartan 3.1 package,<sup>23</sup> obtaining the data given in Table 1. For the  $\alpha$ -diamide assembly, enlargement from a five-membered (**2a**) to a six-membered ring (**3**) has a deshielding effect comparable to those due to enlargement from a five- to a seven-membered ring (**4**) and to variation of the torsional angle  $\theta$  from  $0^\circ$  to almost perpendicular. In lactams,<sup>18</sup> annulation effects vary with the size of the ring. The  $\Delta\delta$  differences for the five- compared with six- or seven-membered ring are 19.5 and 35.0 ppm, respectively. If such had been the case with  $\alpha$ -diamides, the shift difference between **3** and **4** should have been roughly 30–40 ppm. In the case of  $\alpha$ -diketones, there seems to be no such effect. A tentative explanation could perhaps be found in a severe distortion of the rings in the cyclic  $\alpha$ -diamides, as shown in Fig. 1.

It is, in any case, clear enough from the discussed data that variation of the intercarbonyl dihedral angle  $\theta$  has an opposite effect for  $\alpha$ -diketones and  $\alpha$ -diamides. According Cerfontain *et al.*,<sup>3a</sup>  $\theta$  changes have an influence



**Figure 1.** Preferred conformations (hydrogen atoms not shown) of compounds **3** and **4**, as obtained by AM1 calculations.

mainly on the  $\Delta E$  term of the Karplus–Pople equation,<sup>24</sup> and this term is usually approximated to the  $n \rightarrow \pi^*$  forbidden transition in UV spectroscopy. Unfortunately, in the case of  $\alpha$ -diamides, such a transition is difficult to observe and it is assumed<sup>20</sup> to be not resolvable when  $\theta = 90^\circ$ . We too failed to observe it in all the compounds studied. Semi-empirical CNDO/s-CI computations, as reported by Larson and McGlynn,<sup>20</sup> estimated a shift to shorter wavelengths for this transition, when  $\theta = 90^\circ$ , relative to all other  $\alpha$ -diamides. <sup>17</sup>O NMR shifts should therefore have shown a trend similar to that constantly observed<sup>3a,d</sup> for  $\alpha$ -diketones. We do not have a rationale for this observation. Further studies are actively in progress in our laboratories to obtain some insight into this problem.

Compound **1e**, assuming a preferred *s-trans* conformation for the two carbonyl groups, can exist as a mixture of three conformers due to slow (on the NMR time-scale) rotation around the C–N bonds. Namely, calling *c* a situation where a methyl group is *s-cis* to the oxygen atom of its amide group and *t* the opposite situation when it is *s-trans*, we have two different oxygen atoms for the *c/t* conformer and one for each of the two conformers *c/c* and *t/t*. The same number of signals should, of course, be observed for the methyl groups in <sup>1</sup>H and <sup>13</sup>C NMR. Owing to the lack of sensitivity of <sup>17</sup>O NMR spectroscopy, particularly when compared with <sup>1</sup>H NMR, we observed only two signals in our <sup>17</sup>O NMR spectrum and therefore decided to check our results by <sup>1</sup>H NMR. The pertinent <sup>1</sup>H NMR data are given in Table 2.

A <sup>1</sup>H NMR spectrum of **1e** obtained in CDCl<sub>3</sub> solution gave, for the methyl groups, a set of three signals, two of equal intensity at 3.26 and 3.44 ppm and a more intense signal at 3.05 ppm. From the integrals, their relative intensity could be estimated as 23 and 77% for the pair and the intense signal, respectively. In DMSO-*d*<sub>6</sub> all four possible signals were observed and, at room temperature,

**Table 2.**  $^1\text{H}$  NMR Me shifts and populations of conformations of **1e** in  $\text{CDCl}_3$  and  $\text{DMSO}-d_6$ 

Conformer	$\text{CDCl}_3$		$\text{DMSO}-d_6$	
	Shift (ppm)	Population (%)	Shift (ppm)	Population (%)
<i>c/c</i>	3.05	77	2.97	45
<i>c/t</i>	3.26; 3.44	23	3.25, 3.35	51
<i>t/t</i>	Not obs.	—	3.43	4

there were a small signal at 3.43 ppm, a pair at 3.35 and 3.25 ppm and an intense signal at 2.97 ppm. Their relative intensities were *ca* 4, 51 and 45%, respectively. As the pair can be unambiguously assigned at the *c/t* conformer, we observe that this conformation is the most populated in the more polar (dielectric constant  $\text{DMSO}$ ,  $\epsilon = 46.45$ )<sup>25</sup> solvent  $\text{DMSO}-d_6$ . On the other hand, in  $\text{CDCl}_3$  (dielectric constant  $\text{CHCl}_3$ ,  $\epsilon = 4.806$ )<sup>25</sup> *c/t* is roughly one third of the only other conformer still present. MMX calculations<sup>21</sup> allow an estimation of the relative energies and of the dipole moments. The most stable (*in vacuo*) conformer has been computed to be *c/c*, the *c/t* conformer being  $1.45 \text{ kcal mol}^{-1}$  higher in energy. The *t/t* conformer is  $1.24 \text{ kcal mol}^{-1}$  higher up in energy. Their respective dipole moments were computed as 1.43, 1.98 and 2.69 D. We therefore think that the *c/c* conformer is the most populated in  $\text{CDCl}_3$  solution, owing to it having the lowest dipole moment and an energy difference from the *t/t* conformer of  $2.69 \text{ kcal mol}^{-1}$ . The *t/t* conformer, which is the most energetic and has the largest dipole moment, should be that observed only in  $\text{DMSO}-d_6$  at 4%. Owing to this low percentage, we could estimate the rotational barrier around the amide bond only for the two more populated conformers. By total line shape analysis of a  $\text{DMSO}-d_6$  solution spectrum at  $80^\circ\text{C}$ , we obtained  $\Delta G^\ddagger = 18.6 \text{ kcal mol}^{-1}$ , in good agreement with literature data<sup>26</sup> for  $\alpha$ -diamides.

The assignment of the two signals observed by  $^{17}\text{O}$  NMR spectroscopy is tentative. We can reasonably assume that in MeCN solution we have also two main conformers, *c/c* and *c/t*. The third conformer, *t/t*, is

insufficiently populated to be observed by  $^{17}\text{O}$  NMR. We should, however, have observed three signals instead of the two actually measured. The most likely interpretation of this observation is that the resolution in  $^{17}\text{O}$  NMR is not sufficient to discriminate between a *cis*-oxygen in the *c/t* conformer and a *cis*-oxygen in the *c/c* conformer.

The intercarbonyl dihedral angle  $\theta$  has been estimated, by MMX calculations,<sup>21</sup> to be close to  $135^\circ$  and very similar for all three conformers.

## EXPERIMENTAL

The compounds studied were all known, except **1c** and **1d**, and were either purchased (**1a**) or obtained by literature methods (**1b**,<sup>13</sup> **1e**,<sup>6a</sup> **2a,b**,<sup>6b</sup> **2c-i**,<sup>6a</sup> **3**, **4**<sup>27</sup>).

Compounds **1c**, *N,N'*-di-*tert*-butyloxalamide, and **1d**, *N,N'*-di-1-adamantyloxalamide, were prepared by reaction of oxalyl chloride and the respective amine, as described.<sup>20</sup> Their spectroscopic data and elemental analysis results are given in Table 3.

$^{17}\text{O}$  NMR spectra were recorded at 40.662 MHz in the Fourier transform mode on a Varian VXR-300 spectrometer, equipped with a Sun 3/60 computer and with a 10 mm broadband probe, at 338 K and at natural isotopic abundance. Concentrations were, in most cases, of the order of 30–50 mg per 3 ml, owing to the low solubility of  $\alpha$ -diamides. The number of scans was thus up to  $2 \times 10^6$ . The signals were referenced to external deionized water by the substitution method. The instrumental settings were similar to those reported pre-

**Table 3.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR data and elemental analysis results for derivatives **1c** and **1d**

Compound	$^1\text{H}$ NMR shifts <sup>a</sup>	$^{13}\text{C}$ NMR shifts <sup>b</sup>	Calculated (%)	Found (%)
<b>1c</b>	7.73 (NH, 2H); 1.31 (CH <sub>3</sub> , 18 H)	159.21 (C=O); 50.37 (CMe <sub>3</sub> ); 17.71 (CMe <sub>3</sub> )	C59.97, H10.07, N13.99	C59.63, H10.21, N14.12
<b>1d</b> <sup>c</sup>	7.52 (NH, 2H); 2.03 (H <sub>γ</sub> , 6H); 1.97–1.95 (H <sub>β</sub> , 12H); 1.65–1.63 (H <sub>δ</sub> , 12H);	159.02 (C=O); 50.93 (C-1); 40.14 (C-2); 35.52 (C-4); 28.48 (C-3)	C74.12, H9.05, N7.86	C73.97, H9.12, N7.95

<sup>a</sup> Solvent  $\text{DMSO}-d_6$ , room temperature (**1c**) and  $50^\circ\text{C}$  (**1d**), ppm from HMDS internal reference.

<sup>b</sup> Solvent  $\text{DMSO}-d_6$ ,  $40^\circ\text{C}$  (**1c**) and  $50^\circ\text{C}$  (**1d**), ppm from HMDS internal reference.

<sup>c</sup> Assignments for  $^1\text{H}$  and  $^{13}\text{C}$  NMR according to Refs 28 and 29, respectively.

viously.<sup>2</sup> The reproducibility of the chemical shift data is estimated to be  $\pm 1$  ppm.

### Acknowledgements

We thank Professor L. Lunazzi (Bologna University) for the dynamic NMR measurements and helpful discussions and Professor G. Saba (Cagliari University) for AM1 calculations and helpful discussions. Financial support from MURST (60% and 40% funds, 1995–97, to A.G.G., G.C. and G.V.) and CNR (to A.G.G., 1995–97) is gratefully acknowledged.

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