# Distortion of the amide bond in amides and lactams. Photoelectron-spectrum and electronic structure of 3,5,7-trimethyl-1-azaadamantan-2-one, the most twisted amide

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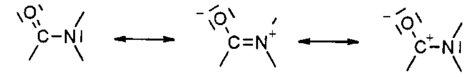
We report the He(I) photoelectron spectrum of 3,5,7-trimethyl-1-azaadamantan-2-one (**20**). Ionization potentials have been assigned to molecular orbitals on the basis of quantum chemical calculations. Compared with other lactams (**1**–**19**), the first ionization, IP[n(N)], of **20** has an usually low energy, while the second, IP[n(O)], appears at a "normal" value. For undistorted lactams, there is a linear correlation of IP[n(O)] values and normalized carbonyl frequencies $\nu_{120}$(C=O): the data for **20** fall well off this correlation. The deformations of the amide linkage in **20**, in the essentially undistorted δ-lactam **9**, the moderately distorted α-lactam **17** and in the bicyclic lactam **19** were investigated by B3LYP/6-31+G* calculations. The deviation from the linear IP[n(O)]/$\nu_{120}$(C=O) correlation can be related to the overall distortion parameter $\theta$ (defined as the sum of the absolute values of the C–N torsional angle $\tau$ and the out-of-plane bending deformations at the amino and the carbonyl group $\chi_N$ and $\chi_C$, respectively). This allows $\theta$ for amides and lactams to be estimated from the observed IP[n(O)] and $\nu$(C=O) values.

## Introduction

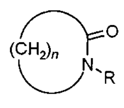
The amide bond is of fundamental interest in structural organic and biological chemistry.[1] The conjugation of the nitrogen lone-pair with the C=O double bond is conveniently described in terms of resonance between two Lewis structures **I** and **II** (Scheme 1).[2] Optimal conjugation requires planarity of the CO–N unit, including its directly bound neighbours. This delocalization leads to a weakening of the C=O bond, reflected in a low carbonyl stretching vibrational frequency $\nu$(C=O), and a strengthened C–N bond with partial double bond character, reflected in hindered internal rotation. Twisting or other distortion of the amide group inhibits this delocalization and thus modifies the electronic structure and chemical properties of the group. Relationships have been identified between the twist angle and various spectroscopic properties, including $\nu$(C=O), $^{13}$C, $^{15}$N and $^{17}$O chemical shifts.[3] The properties of nonplanar amides and lactams have been reviewed recently by Greenberg.[4,5]


I II III

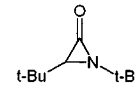
**Scheme 1**

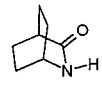
Although the resonance model of amides[2] has been generally accepted, it has been challenged by Wiberg *et al.*[6,7] on the basis of comparisons of the calculated C, N, O electron densities of planar and twisted amides. Significantly, while distortion of the amide linkage introduces large variations in the CO–N bond length, the bond length of the carbonyl group is hardly changed. In an attempt to rationalize these results, a third resonance structure, **III**, was introduced, so that the dominant structures representing an amide become **II** and **III**. This implies that the carbonyl group in amides is best written as $C^+$–$O^-$. However, the polarity of the CO bond is considerably lower than that of ketones.

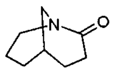
Amides have three π type MOs ($\pi_1$–$\pi_3$) of which two are occupied. These can be classified qualitatively as $\pi_1 \approx \pi$(C=O) and $\pi_2 \approx \pi$(N). In addition, there is an oxygen lone-pair orbital n(O) among the high-level MOs. Analysis of the electronic structure of secondary and tertiary lactams **1**–**19**[8] by UV photoelectron (PE) spectroscopy reveals a linear correlation between the ionization potential related to the n(O) orbital, IP[n(O)], and the normalized $\nu_{120}$(C=O) (frequency corrected for angle strain) of the carbonyl vibration. $\nu_{120}$(C=O) Values correspond to a hypothetical C–CO–N bond angle $\alpha$ of 120°, obtained from the observed frequencies $\nu$(C=O) and bond angles $\alpha$ using eqn. (1) derived by Cook.[9]

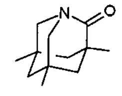


| n | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|---|---|---|---|---|---|---|---|---|---|---|
| R = H | **1** | **2** | **3** | **4** | **5** | **6** | | | | |
| R = CH$_3$ | **7** | **8** | **9** | **10** | **11** | **12** | **13** | **14** | **15** | **16** |


**17**


**18**


**19**


**20**

$$\nu_{120}(\text{C=O}) = 96\,[\nu(\text{C=O}) - 1439]/(216 - \alpha) + 1439\ [\text{cm}^{-1}] \quad (1)$$

Previous investigations have shown that compounds with a twisted or distorted amide bond diverge from the linear correlation between IP[n(O)] and $\nu_{120}$(C=O) [eqn. (2)].[8,10] Two

$$\nu_{120}(\text{C=O}) = 57.81\ \text{IP[n(O)]} + 1117.8\ [\text{cm}^{-1}]\ (n = 17,\ r = 0.978) \quad (2)$$

**Table 1** Ionization potentials IP and orbital energies $\varepsilon$ of 3,5,7-trimethyl-1-azaadamantan-2-one (**20**)

| | | | B3LYP/6-31+G* | | | |
|---|---|---|---|---|---|---|
| $IP_v$/eV | PM3 $-\varepsilon$/eV | AM1 $-\varepsilon$/eV | $IP_a$/eV | $IP_v$/eV | $-\varepsilon$/eV | |
| 8.30[a] | 9.44 | 9.34 | 7.64[b] | 8.02[c] | 6.16 | n(N) |
| 9.45 | 10.83 | 10.92 | | 9.00[d] | 7.14 | n(O) |
| 10.27 | [e] | [e] | | | [e] | $\sigma$ |
| 11.30 | [e] | [e] | | | [e] | $\sigma$ |
| 12.1 | [e] | [e] | | | [e] | $\sigma$ |
| 13.1 | 13.24 | 13.10 | | 12.17[d] | 10.31[e] | $\pi$(C=O)/$\sigma$ |

[a] $IP_a$ = 7.78 eV. [b] Energy difference of molecule (−598.7243504 au) and radical cation (−598.4436344 au). [c] Energy difference of molecule (−598.7243504 au) and radical cation with geometry of molecule (−598.4295308 au). [d] Estimated from the corresponding $\varepsilon$ value by addition of 1.86 eV (see text). [e] There are about 8 $\sigma$ levels in this region.

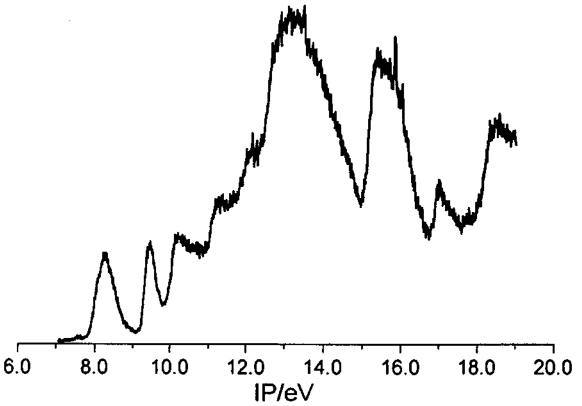


**Fig. 1** PE spectrum of azaadamantanone **20**.

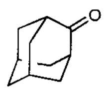
prominent examples which show a marked divergence are 1,3-di-*tert*-butylaziridin-2-one (**17**) and 1-azabicyclo[3.3.1]nonan-2-one (**19**).

3,5,7-Trimethyl-1-azaadamantan-2-one[11] (**20**) has recently become available. The properties of **20** indicate that it is the most twisted amide, *i.e.* the nitrogen electron lone-pair is coplanar with the C=O group. We report the electronic structure, obtained by PE spectroscopy, and relevant quantum chemical calculations for this unique—and remarkably stable—compound. Since our main interest was to discover how the degree of deformation of an amide or a lactam is related to its characteristic IPs and carbonyl frequency, we have included in our study 1-methylpiperidin-2-one (**9**) as an essentially undistorted lactam, and compounds **17** and **19** as two moderately distorted lactams.

## PE spectrum and electronic structure of azaadamantanone 20

The PE spectrum of **20** is depicted in Fig. 1. The relevant IP values are listed in Table 1 together with the results of quantum chemical calculations. Based on the results of various theoretical methods like AM1,[12] PM3[13] and B3LYP,[14–16] the first ionization potential is assigned to the removal of an electron from the nitrogen lone-pair MO, n(N), and the second IP is assigned to the analogous process related to the n(O) orbital. Compared with other tertiary lactams, the first IP of **20** appears at an unusually low energy, about 0.6 eV lower than in 1-methylpiperidin-2-one (**9**). The n(N) ionization of **20** is, however, 0.36 eV higher than that of 1-azaadamantane (**21**).[17] The stabilization of this orbital in **20** is obviously caused by the inductive effect of the carbonyl group.

**21**



**22**

In contrast, the second IP of **20**, IP[n(O)], is shifted by only about 0.1 eV to higher energy relative to the value for **9**. This small difference no doubt results from a combination of factors. The inhibition of the n(N)–$\pi$*(C=O) interaction in **20** stabilizes n(O) and thus raises IP[n(O)]. On the other hand the radical cation will be relatively more stable, and thus the IP lowered for **20**, simply because larger molecules stabilize charge more effectively [compare IP[n(O)] for **9** with values for larger-ring tertiary lactams **10**–**16** (Fig. 2), where the size effect has more or less levelled out]. Compared with adamantanone (**22**, IP value 8.80 eV[17]) it seems clear that n(O) is significantly stabilized.

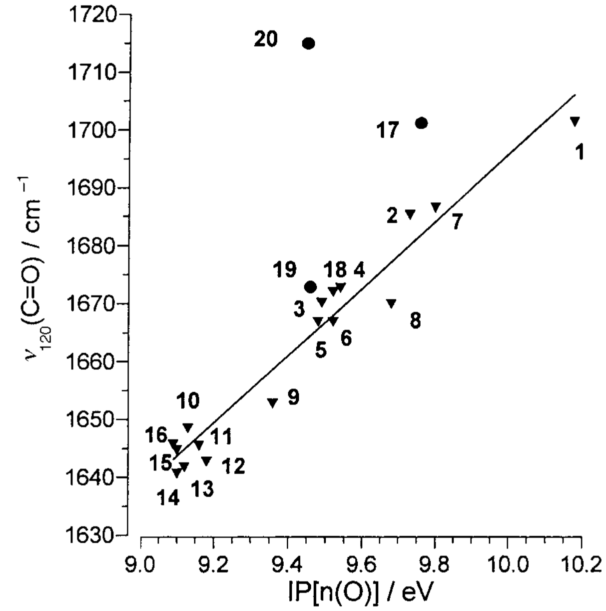


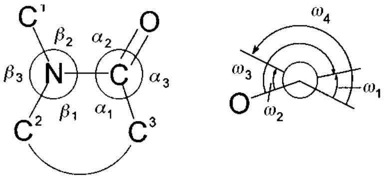
**Fig. 2** Correlation of ionization potentials IP[n(O)] with normalized carbonyl frequencies $\nu_{120}$(C=O) for compounds **1**–**20**.

As a consequence of the semiempirical methodology, the orbital energies $\varepsilon$ calculated by AM1 and PM3 are too low by 1.0–1.5 eV, whereas for the B3LYP method they are too high by about 2 eV (Table 1). However, all three methods lead to the same assignment of the IPs, using the Koopmans theorem $IP_i = -\varepsilon_i$.[18] Much better agreement between experimental and theoretical values is reached for the first adiabatic and vertical IP ($IP_a$, $IP_v$) when the energies of the molecule and the radical cation are calculated by the B3LYP method. For $IP_v$ a single point calculation was performed for the radical cation using the molecule's geometry, while for $IP_a$ the structure of the latter species was optimized. The corresponding energy values are given in Table 1. We can now correct other B3LYP $\varepsilon$ values by the difference $\Delta$ = 1.86 eV between $-\varepsilon$(HOMO) and the calculated $IP_v$ value of the first IP in order to obtain higher $IP_v$ values. In this way a value of 9.00 eV is obtained for IP[n(O)] which compares well to that found experimentally (Table 1).

Fig. 2 shows the relationship between IP[n(O)] and $\nu_{120}$(C=O) for various secondary and tertiary lactams (**1**–**19**). Azaadamantanone **20** has a carbonyl frequency of 1732 cm$^{-1}$[11] from which $\nu_{120}$(C=O) = 1716.4 cm$^{-1}$ is obtained by eqn. (1) with $\alpha$ = 114.6°. As expected, the point for **20** in Fig. 2 falls well off the straight line confirming that **20** is better described as an aminoketone than a lactam or amide.

## Distortion of the amide linkage

Out-of-plane deformations of the amide group from the stable planar form involve the pyramidalization of the amino group and/or twisting around the CO–N bond, which may be accompanied by pyramidalization of the carbonyl carbon atom. For a quantitative description of the degree of distortion at least two parameters are necessary: a twist angle $\tau$ derived from the torsion angles $\omega_1$ and $\omega_2$, and the sum $\Sigma\beta$ of the bond angles at the nitrogen atom (Scheme 2). $\tau = 0°$ and $\Sigma\beta = 360°$ thus correspond to an undistorted amide group while maximal distortion as in compound **20**[11] is described by $\Sigma\beta = 328°$ (*i.e.* $\beta \ll 360°$) and $\tau = 90°$. In addition to the CO–N twist angle $\tau$, Winkler and Dunitz[19–21] introduced the parameters $\chi_N$ and $\chi_C$, to represent the pyramidality at nitrogen and carbon, respectively. These parameters are defined in Scheme 2. Other indicators for inhibited amide resonance are of course the lengths of the C=O and C–N bonds.



$C^3$–C–N–$C^2$ = $\omega_1$ $\quad$ $\tau = ½ (\omega_1 + \omega_2)$

O=C–N–$C^1$ = $\omega_2$ $\quad$ $\chi_C = \omega_1 - \omega_3 + \pi = \omega_4 - \omega_2 + \pi$

O=C–N–$C^2$ = $\omega_3$ $\quad$ $\chi_N = \omega_2 - \omega_3 + \pi = \omega_4 - \omega_1 + \pi$

$C^3$–C–N–$C^1$ = $\omega_4$

**Scheme 2** Bond angles $\alpha$ and $\beta$, torsion angles $\omega$, and distortion parameters $\tau$, $\chi_C$ and $\chi_N$.

If we use the carbonyl frequency $\nu$(C=O) and the n(O) ionization potential of a particular amide or lactam to investigate the distortion of the amide group, we can estimate an "overall distortion" using Fig. 2. However, exact values of individual distortion parameters cannot be obtained in this way. As a measure of the overall distortion of an amide linkage we define the parameter $\theta$ as the sum of the absolute values of $\tau$, $\chi_C$ and $\chi_N$ [eqn. (3)]. Since we do not know how the individual

$$\theta = |\tau| + |\chi_C| + |\chi_N| \qquad (3)$$

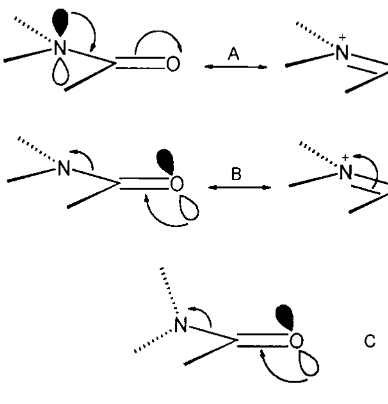
distortion parameters affect $\nu$(C=O) and IP[n(O)], this approach is only approximate.

To assess and compare degrees of nonplanarity in lactams we have investigated the molecular structures of compounds **9**, **17**, **19** and **20** by various theoretical methods. To our knowledge, only the structure of **20** has been determined by X-ray analysis. For a quantitative study it is essential that the structures of the compounds are determined by the same method. For this purpose we use the data computed by the B3LYP method using the basis set 6-31+G*. Data calculated with methods of lower sophistication like MMX, AM1 and PM3 were rejected: for some compounds rather similar structures were obtained, but some structure parameters were substantially divergent for all these methods. The relevant structural parameters are summarized in Table 2. The calculated structure parameters of **20** compare well with those from the X-ray analysis.[11] For all four compounds, the carbonyl group is essentially planar: the sum $\Sigma\alpha$ of the bond angles at the carbonyl carbon atom deviates—if at all—only marginally from 360°. Our results regarding the structural changes caused by distortion are in accordance with the findings of Wiberg *et al.*[6,7] mentioned above.

**Table 2** Selected structural parameters, ionization potentials IP and normalized carbonyl frequencies $\nu_{120}$(C=O) of lactams **9**, **17**, **19** and **20** from B3LYP/6-31+G* calculations

| | **9** | **17** | **19** | **20** |
|---|---|---|---|---|
| C=O/pm | 123.2 | 121.3 | 122.6 | 121.0 |
| C–N/pm | 137.5 | 134.3 | 139.6 | 145.5 |
| $\alpha_1$/° | 117.8 | 64.8 | 113.8 | 114.1 |
| $\alpha_2$/° | 122.2 | 144.0 | 122.6 | 121.5 |
| $\alpha_3$/° | 119.9 | 150.8 | 123.2 | 124.4 |
| $\Sigma\alpha$/° | 359.9 | 359.6 | 359.6 | 360.0 |
| $\beta_1$/° | 124.7 | 62.1 | 114.4 | 109.0 |
| $\beta_2$/° | 119.0 | 132.2 | 115.2 | 109.0 |
| $\beta_3$/° | 115.2 | 133.7 | 111.3 | 110.0 |
| $\Sigma\beta$/° | 358.9 | 328.0 | 340.9 | 328.0 |
| $\omega_1$/° | 9.8 | 0.0 | 131.0 | 60.0 |
| $\omega_2$/° | −4.8 | −47.9 | 187.3 | −120.0 |
| $\omega_3$/° | −172.8 | −173.0 | −41.9 | 120.0 |
| $\omega_4$/° | 177.8 | 125.1 | 0.2 | 60.0 |
| $\tau$/° | 2.5 | −24.0 | −20.9 | −90.0 |
| $\chi_C$/° | 2.6 | −7.0 | −7.1 | 0.0 |
| $\chi_N$/° | −12.0 | −54.9 | 49.2 | −60.0 |
| $\theta$/° | 17.1 | 85.9 | 77.2 | 150.0 |
| IP[n(O)]/eV | 9.36 | 9.76 | 9.46 | 9.45 |
| $\nu_{120}$(C=O)/cm$^{-1}$ | 1653 | 1701 | 1673 | 1715 |

**Bond lengths.** The data in Table 2 show that the bond length of the carbonyl group $r$(C=O) varies very little with the distortion of the amide group ($\Delta r$ = 2.2 pm). On the other hand there is a very substantial increase in the length of the CO–N bond in **20** (145.5 pm) compared with that in a simple tertiary δ-lactam **9** (137.5 pm) and 139.6 for the less distorted **19**. We take this as an indication that only almost complete inhibition of amide resonance will lead to a "normal" C–N single bond length. It is noteworthy that although the length of the CO–N bond, the ionization energy of the oxygen electron lone-pair IP[n(O)] and the carbonyl frequency $\nu$(C=O) are all rather sensitive to distortions of the amide linkage, this is not the case for the bond length $r$(C=O).



**Scheme 3** Orbital interactions.

This may be explained in terms of the separate stereoelectronic interactions of neighbouring orbitals in and out of the plane of the carbonyl group, which have opposite effects on bond lengths. The familiar n(N)–π*(C=O) overlap (**A**, Scheme 3), leads to shortening and strengthening of the C–N bond, which acquires some double bond character, and to a lesser extent (because the bond is shorter to start with) lengthening of C=O. In the plane, acting independently because the orbitals are orthogonal to the π-system, and in the opposite sense, is an n(O)–σ*(C–N) interaction (**B**). This is the same type of interaction involved in the anomeric effect, and responsible for the well-known shortening of the central C–O bonds of acetals.[22] It operates to some extent in all carboxylic acid derivatives, so that the C=O bond lengths differ very little from those of ketones: even for carboxylate anions (125 compared with 121 pm).[23] In compound **20** the geometry of the bicyclic system precludes π- or σ-type donation from the nitrogen lone-pair, so only the n(O)–σ*(C–N) interaction (**C**) remains. The result is a C=O bond slightly shorter than in a typical ketone [119.7(4) compared with 121 pm]. The ionization potential IP[n(O)] is higher than for the comparable adamantanone (9.45 compared with 8.80 eV, see above) for the same reason.

**Distortion from planarity.** The distortion parameters listed in Table 2, in particular $\tau$, $\chi_N$ and $\theta$, indicate that in the δ-lactam **9** ($\theta = 17.1°$) the amide linkage is—as expected—essentially undistorted, whereas in the α-lactam **17** ($\theta = 85.9°$) and the bicyclic lactam **19** ($\theta = 63.6°$) it is clearly, but only moderately, distorted. In **9** only the out-of-plane bending of the amino group ($\chi_N$) is significantly different from 0°: the sum $\Sigma\beta$ of the bond angles at the nitrogen atom deviates only by 1.1° from 360°. It is noteworthy that for **17** and **19** the distortion is mainly caused by the high degree of pyramidalization of the nitrogen atom. For the most twisted azaadamantanone **20** ($\theta = 150.0°$) the overall distortion is nearly twice as large as for **17**, and both the torsion angle $\tau$ and the nitrogen pyramidality $\chi_N$ supply a large contribution.

We can now correlate the overall distortion parameter $\theta$ with the deviation of the points for compounds **9**, **17**, **19** and **20** using the line in Fig. 2. [It is important to use the bond angles $\alpha_1$ obtained by the B3LYP calculations (Table 2) for the calculation of $\nu_{120}$(C=O): in a previous investigation[8] structure parameters of different origin including MNDO results were used.] In this way a "normal" IP[n(O)] of 10.33 eV is calculated from the observed carbonyl frequency of **20** using eqn. (4) [which follows from eqn. (2)].

$$\mathrm{IP[n(O)]} = 0.0173\ \nu_{120}(\mathrm{C{=}O}) - 19.34\ [\mathrm{eV}] \qquad (4)$$

Alternatively, using the observed IP[n(O)] value gives a calculated value for the carbonyl frequency [eqn. (2)] of 1664 $\mathrm{cm}^{-1}$, much lower than that observed. Thus **20** has a much lower IP[n(O)] ($\Delta\mathrm{IP} = +0.88$ eV) or a much higher $\nu_{120}$(C=O) ($\Delta\nu = -51\ \mathrm{cm}^{-1}$) compared with an undistorted lactam. For the two moderately distorted lactams the corresponding Δ values are: **17** $\Delta\nu = -19\ \mathrm{cm}^{-1}$ and $\Delta\mathrm{IP} = +0.33$ eV, **19** $\Delta\nu = -9\ \mathrm{cm}^{-1}$ and $\Delta\mathrm{IP} = +0.14$ eV; for the undistorted lactam **9** $\Delta\nu = +6\ \mathrm{cm}^{-1}$ and $\Delta\mathrm{IP} = -0.10$ eV are calculated. Comparison of these Δ values with the "overall distortion" $\theta$ (Table 2) gives reasonable linear

$$\theta = 126.9\ \Delta\mathrm{IP[n(O)]} + 42.9\ [°]\ (n = 4, r = 0.975) \qquad (5)$$

$$\theta = -2.20\ \Delta\nu_{120}(\mathrm{C{=}O}) + 42.3\ [°]\ (n = 4, r = 0.977) \qquad (6)$$

correlations [eqns. (5) and (6)]. From these equations it is possible to estimate the overall distortion of an amide or lactam from its n(O) ionization potential and carbonyl frequency.

## Experimental

The PE spectrum of compound **20** was recorded at 100 °C on a Leybold-Heraeus UPG200 spectrometer equipped with a He(I) radiation source (21.21 eV). The energy scale was calibrated with the lines of xenon at 12.130 and 13.436 and of argon at 15.759 and 15.937 eV. The accuracy of the measurements was approximately ±0.03 eV for ionization energies; for broad and overlapping signals it was only ±0.1 eV.

Semiempirical AM1[12] and PM3[13] calculations were performed with the MOPAC93[24] program package, Becke3LYP[14–16] calculations with the program GAUSSIAN 94.[25] Geometries were fully optimized at the respective levels of theory.

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## References

1 A. Greenberg, C. Breneman and J. F. Liebman (eds.), *The Amide Linkage: Structural Significance in Chemistry, Biochemistry and Material Science*, Wiley, New York, 1999 (in the press).
2 L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, NY, 1960.
3 S. Yamada, *J. Org. Chem.*, 1996, **61**, 941.
4 A. Greenberg, in *Structure and Reactivity*, eds. J. L. Liebman and A. Greenberg, VCH Publ., New York, 1988, ch. 4, p. 139.
5 A. Greenberg, in *The Amide Linkage: Structural Significance in Chemistry, Biochemistry and Material Science*, eds. A. Greenberg, C. Breneman and J. F. Liebman, Wiley, New York, 1999, ch. 3 (in the press).
6 K. B. Wiberg and K. E. Laidig, *J. Am. Chem. Soc.*, 1987, **109**, 5935.
7 K. B. Wiberg and C. M. Breneman, *J. Am. Chem. Soc.*, 1992, **114**, 831.
8 L. Treschanke and P. Rademacher, *J. Mol. Struct.* (*THEOCHEM*), 1985, **122**, 47.
9 D. Cook, *Can. J. Chem.*, 1961, **39**, 31.
10 P. Rademacher, in *The Amide Linkage: Structural Significance in Chemistry, Biochemistry and Material Science*, eds. A. Greenberg, C. Breneman and J. F. Liebman, Wiley, New York, 1999, ch. 9 (in the press).
11 A. J. Kirby, I. V. Komarov, P. D. Wothers and N. Feeder, *Angew. Chem.*, 1998, **110**, 830; *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 785.
12 M. J. S. Dewar, E. G. Zoebisch, H. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902.
13 J. J. P. Stewart, *J. Comput. Chem.*, 1989, **10**, 209, 221.
14 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.
15 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 1372.
16 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
17 C. Worrell, J. W. Verhoeven and W. N. Speckamp, *Tetrahedron*, 1974, **30**, 3525.
18 T. Koopmans, *Physica*, 1934, **1**, 104.
19 F. K. Winkler and J. D. Dunitz, *J. Mol. Biol.*, 1971, **59**, 169.
20 J. D. Dunitz and F. K. Winkler, *Acta Crystallogr., Sect. B*, 1975, **31**, 251.
21 J. D. Dunitz, *X-Ray Analysis and the Structure of Organic Molecules*, Cornell University Press, Ithaca, 1979.
22 A. J. Kirby, *The Anomeric Effect and Related Stereoelectronic Effects at Oxygen*, Springer Verlag, Berlin and Heidelberg, 1983.
23 F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, S1.
24 J. J. P. Stewart, *MOPAC93.00 Manual*, Fujitsu Limited, Tokyo, Japan, 1993.
25 M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, *Gaussian 94, Revision E.2*, Gaussian, Inc., Pittsburgh, PA, 1995.

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