13. The Structure of 1*H*-Perimidin-2(3*H*)-one and Its Derivatives in the Solid State (X-Ray Crystallography and CP/MAS ^{13}C-NMR), in Solution (^{13}C-NMR), and in the Gas Phase (Mass Spectrometry)

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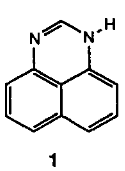
The X-ray crystal and molecular structures of 1-methyl-1*H*-perimidin-2(3*H*)-one (**5b**) and 1,3-dimethyl-1*H*-perimidin-2(3*H*)-one (**6**) were determined. The crystals are built of piles of dimers faced head-to-head in **5b** and of alternating independent head-to-tail molecules in **6**, both along the *b* axis. Semiempirical calculations at the AM1 level revealed that the eclipsed conformation of the Me groups with respect to the C=O group, found in the crystals, is the most stable. The lack of planarity of the whole molecules is a consequence of the packing forces since it is not found in the calculations. A comparative NMR study was carried out in solution (^{1}H and ^{13}C) and in the solid state (CP/MAS ^{13}C) for 1*H*-perimidin-2(3*H*)-one (**2**) and 1*H*-benzimidazol-2(3*H*)-one (**3**) with the conclusion that in both heterocycles the oxo tautomer is the most abundant. The structure in the gas phase was approached by mass spectrometry. In the case of **3**, the oxo tautomer loses CO after ionization, while the oxo form of **2** tautomerizes to the hydroxy form which loses H_2O after a [1,3]-H shift. AM1 calculations were carried out on the ground and ionized states of **2**.

1. Introduction. – The 1*H*-perimidine (**1**) is an interesting heterocyclic system: owing to the fusion of three six-membered rings, it is aromatic and, at the same time, presents



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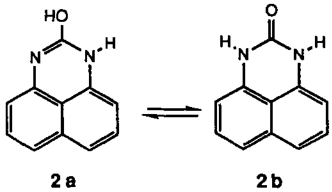
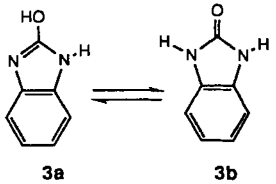
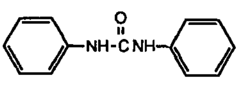


2a **2b**



3a **3b**



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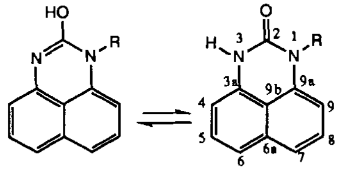
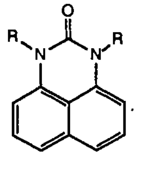
annular tautomerism [1], an almost unique situation in six-membered heterocyclic compounds. Its 2-hydroxy derivative **2a** exists in equilibrium with the oxo form **2b**. This cyclic urea is related both to 1*H*-benzimidazol-2(3*H*)-one (**3b**) and to 1,3-diphenylurea (= carbanilide; **4**).

The relative position of the equilibria **2a** $\rightleftharpoons$ **2b** and **3a** $\rightleftharpoons$ **3b** is related to the aromaticity of 1*H*-perimidine (**1**) *vs.* that of 1*H*-benzimidazole. This last compound is clearly aromatic (I_A = 148 [2]), but the aromaticity of **1**, although formally a 14π aromatic system related to phenalenium anion [3], was not clearly assessed. Since benzimidazolone **3b** exists as such and not in the hydroxy form **3a** [4], and since is not expected to be more aromatic than 1*H*-benzimidazole, perimidinone **2b** should be the most stable tautomer. However, *Woodgate et al.* [5] found that although the compound is in the oxo form **2b** at equilibrium, a frehsly prepared solution shows the signals of the hydroxy tautomer **2a**, which implies that this is the tautomer present in the solid state. Later, we confirmed that in solution the major tautomer is indeed the oxo form, but we were unable to repeat *Woodgate*'s experiment [6]. Thus, the problem of the structure of **2** in the solid state as well as that in the gas phase being still unsolved, we decided to carry out a systematic study of **2** and its derivatives in the solid state, in solution and in the gas phase. As model compounds, we chose 1-methyl-1*H*-perimidin-2(3*H*)-one (**5**), 1-ethyl-1*H*-perimidin-2(3*H*)-one (**7**), 1-propyl-1*H*-perimidin-2(3*H*)-one (**9**), the corresponding 1,3-dialkyl derivatives **6**, **8**, and **10**, and 2-methoxy-1-methyl-1*H*-perimidine (**11**).

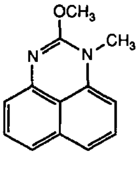


5a R = CH_3
7a R = C_2H_5
9a R = C_3H_7

5b R = CH_3
7b R = C_2H_5
9b R = C_3H_7



6 R = CH_3
8 R = C_2H_5
10 R = C_3H_7



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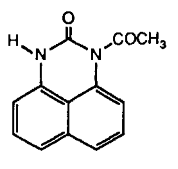

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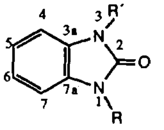
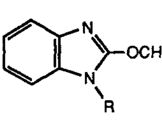
2. Results and Discussion. – *Synthesis.* Perimidinone **2** was prepared according to *Sachs'* procedure [7] from naphthalene-1,8-diamine and urea in HCl, and 1-alkyl- and 1,3-dialkylperimidinones **5**–**10** were obtained by alkylation of **2** with the appropriate alkyl iodide in basic media [8]. The 2-methoxy-1-methyl-1*H*-perimidine (**11**) was synthesized from 2-chloro-1-methyl-1*H*-perimidine [7] and NaOMe. All attempts to isolate 2-methoxy-1*H*-perimidine from the 2-chloro derivative and NaOMe were unsuccessful, due to the easy isomerization of the desired product into 1-methyl-1*H*-perimidin-2(3*H*)-one (**5**). Acetylation of **2** with acetyl chloride yielded 1-acetyl-1*H*-perimidin-2(3*H*)-one (**12**).

The corresponding 1,3-dimethyl-1*H*-benzimidazol-2(3*H*)-one (**14**) was also prepared by direct methylation of **3** [9] with MeI. The 1-methyl and 1-ethyl derivatives **13** and **15**, respectively, were commercial products. The 2-methoxy-1-methyl-1*H*-benzimidazole (**17**) was formed by nucleophilic substitution of the Cl-atom of 1-methyl-2-chloro-1*H*-benzimidazole [10] by MeO^-.



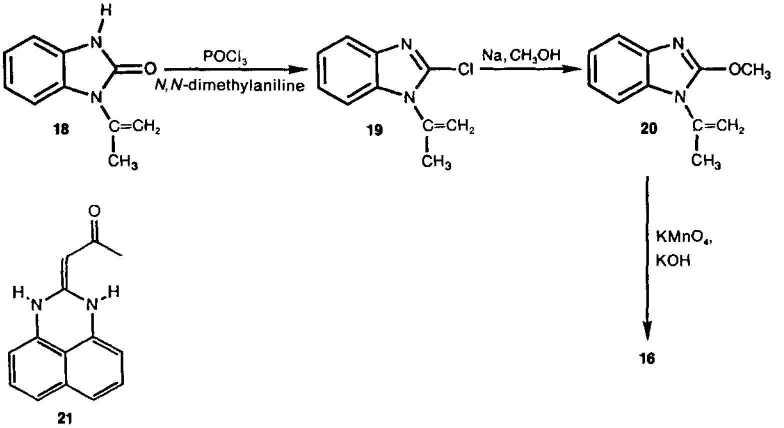
3 R=R'=H
13 R=CH_3, R'=H
14 R=R'=CH_3
15 R=C_2H_5, R'=H



16 R=H
17 R=CH_3

To prepare 2-methoxy-1*H*-benzimidazole (**16**), we used the *Harrison* and *Jones'* method [11] which follows a three-step sequence (*Scheme 1*) starting from 1-isopropenyl-1*H*-benzimidazol-2(3*H*)-one (**18**) prepared from benzene-1,2-diamine and ethyl acetoacetate. All intermediate products were completely characterized by NMR spectroscopy for the first time (*cf. Exper. Part*). When we tried to apply the same reaction to naphthalene-1,8-diamine, the only product isolated in the first step was 3-[(1*H*)-perimidin-2(3*H*)-ylidene]propan-2-one **21** instead of 1-isopropenyl-1*H*-perimidin-2(3*H*)-one.

Scheme 1



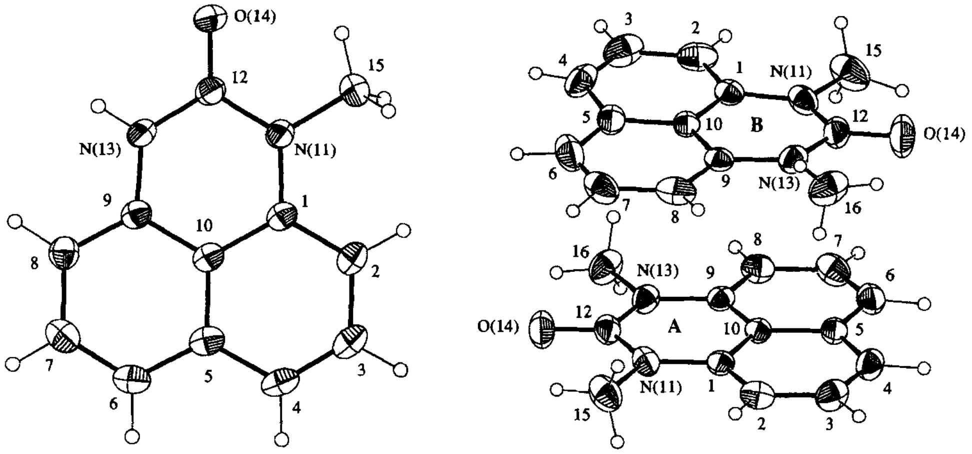
Solid State: X-Ray Crystallography. The geometrical characteristics derived from the crystallographic analysis of compounds **5b** and **6** are given in *Tables 1* and *2*, with the numbering system shown in *Fig. 1*. When the molecular geometry of the naphthalene moiety of **5b** and **6** is compared with that of naphthalene itself [12], some structural changes emerge due to the presence of the third ring linked to the *peri* positions. Without taking into account the bond distances and angles most affected by thermal motion, it is worth noticing the shortening of all distances involving atoms C(5) and C(10) and the decrease of the C(1)–C(10)–C(9) angle. Moreover, in both **5b** and **6**, this moiety is also characterized by a significant lack of planarity ($\chi 2$ values of 539.20, 178.29, and 305.24 for **5b** and molecules A and B of **6**, resp., *vs.* the theoretical value of 14.10). The deformation parameters [13] around the C(5)–C(10) bond show that, although just at the limit of signification (*ca.* 2σ its value), all molecules present similar distortions at both

Table 1. *Selected Bond Distances* [Å] *and Angles* [°]

	5b	**6**			**5b**	**6**	
		Molecule A	Molecule B			Molecule A	Molecule B
C(1)–C(2)	1.379(3)	1.378(6)	1.378(6)	C(1)–C(10)–C(5)	120.6(1)	119.8(3)	119.6(3)
C(1)–C(10)	1.418(2)	1.410(4)	1.413(4)	C(5)–C(10)–C(9)	119.7(1)	119.6(2)	120.7(3)
C(1)–N(11)	1.406(2)	1.401(4)	1.393(5)	C(10)–C(1)–N(11)	118.0(1)	117.4(3)	117.5(3)
C(2)–C(3)	1.406(2)	1.394(5)	1.382(7)	C(2)–C(1)–N(11)	122.3(1)	122.5(3)	122.9(3)
C(3)–C(4)	1.359(3)	1.348(5)	1.339(8)	C(8)–C(9)–N(13)	122.1(2)	122.2(3)	123.1(3)
C(4)–C(5)	1.418(3)	1.414(6)	1.428(6)	C(10)–C(9)–N(13)	117.3(1)	117.4(3)	118.2(3)
C(5)–C(6)	1.413(2)	1.413(4)	1.411 (5)	C(1)–C(10)–C(9)	119.7(1)	120.6(3)	119.8(3)
C(5)–C(10)	1.412(2)	1.417(4)	1.413(5)	C(1)–N(11)–C(12)	123.0(1)	123.7(2)	123.8(3)
C(6)–C(7)	1.368(3)	1.355(7)	1.343(8)	N(11)–C(12)–N(13)	116.9(1)	117.4(3)	117.1(3)
C(7)–C(8)	1.401(2)	1.405(5)	1.403(7)	C(9)–N(13)–C(12)	125.2(1)	123.4(3)	123.3(3)
C(8)–C(9)	1.374(2)	1.374(5)	1.383(5)	N(11)–C(12)–O(14)	121.6(1)	120.9(3)	121.5(3)
C(9)–C(10)	1.415(3)	1.415(6)	1.414(5)	N(13)–C(12)–O(14)	121.5(2)	121.7(3)	121.3(4)
C(9)–N(13)	1.390(2)	1.407(4)	1.385(5)	C(1)–N(11)–C(15)	119.3(1)	118.5(3)	119.0(4)
N(11)–C(12)	1.375(2)	1.372(6)	1.368(6)	C(12)–N(11)–C(15)	117.7(1)	117.7(3)	117.2(3)
C(12)–N(13)	1.355(2)	1.369(4)	1.372(4)	C(12)–N(13)–C(16)	–	118.0(3)	117.5(3)
N(11)–C(15)	1.458(2)	1.464(5)	1.476(5)	C(9)–N(13)–C(16)	–	118.6(3)	119.2(3)
C(12)–O(14)	1.230(2)	1.224(4)	1.229(5)				
N(13)–C(16)	–	1.458(6)	1.466(6)				

Table 2. *Selected Torsion Angles* [°] *and Deformation Parameters X* [°] *Around the C(5)–C(10) Bond*

	5b	**6**	
		Molecule A	Molecule B
N(11)–C(1)–C(10)–C(5)	-178.8(1)	-179.6(3)	-177.8(3)
N(11)–C(1)–C(10)–C(9)	1.6(2)	-0.6(4)	3.1(5)
N(13)–C(9)–C(10)–C(1)	-0.8(2)	1.4(5)	2.0(5)
N(13)–C(9)–C(10)–C(5)	179.7(1)	-179.5(3)	-177.1(3)
C(4)–C(5)–C(10)–C(1)	-0.2(2)	0.2(5)	-2.2(5)
C(6)–C(5)–C(10)–C(1)	-179.7(2)	179.2(3)	178.9(3)
C(6)–C(5)–C(10)–C(9)	-0.2(2)	0.1(5)	-2.0(5)
C(4)–C(5)–C(10)–C(9)	179.3(2)	-178.9(3)	177.0(3)
C(10)–C(1)–N(11)–C(12)	-1.4(2)	-0.6(5)	-4.9(5)
C(1)–N(11)–C(12)–N(13)	0.3(2)	0.9(5)	1.3(5)
N(11)–C(12)–N(13)–C(9)	0.6(2)	0.1(5)	4.3(5)
C(12)–N(13)–C(9)–C(10)	-0.4(2)	-1.2(5)	-5.9(5)
C(1)–N(11)–C(12)–O(14)	-179.2(2)	-179.6(3)	-177.4(4)
C(15)–N(11)–C(12)–O(14)	-1.0(2)	-1.1(5)	2.1(6)
O(14)–C(12)–N(13)–C(9)	-179.9(2)	-179.5(3)	-177.0(4)
O(14)–C(12)–N(13)–C(16)	–	-1.3(5)	3.4(6)
C(10)–C(1)–N(11)–C(15)	-179.5(2)	-179.0(3)	175.7(4)
C(2)–C(1)–N(11)–C(15)	0.4(2)	1.6(5)	-3.2(5)
C(8)–C(9)–N(13)–C(16)	–	0.4(5)	-5.8(5)
C(10)–C(9)–N(13)–C(16)	–	-179.4(3)	173.7(4)
C(12)–N(11)–C(15)–H(151)/H(152)	9(2)	6(4)	4(3)
C(12)–N(13)–C(16)–H(163)/H(161)	–	2(4)	-2(5)
χ_τ	-0.2(1)	-0.2(2)	-2.1(2)
$\chi_{1,9}$	-0.5(3)	0.9(6)	-0.9(6)
$\chi_{4,6}$	-0.5(3)	1.0(6)	-1.1(6)



5b **6**

Fig. 1. *Perspective view of the asymmetric units of compounds* **5b** *and* **6**

ends of the bond ($\chi_{1,9} \approx \chi_{4,6}$). However, the overall twist in molecule B is significantly different from the others.

The two crystallographically independent molecules of **6** are related by a pseudoinversion center (see *Exper. Part*). The main differences between them [14] are confined to the C(9)–N(13) distance and to the puckering of the pyrimidine ring (*Tables 1* and *2*). The total puckering amplitudes [15] are 0.013(3) and 0.053(3) Å in molecule A and B of **6** and 0.013(2) Å in **5b**. Deviations in the intracyclic torsion angles arise from the slightly different environment of the C=O groups, more overcrowding in molecule B than in molecule A (*Table 3*). The Me groups which are in a staggered conformation with respect to C(1)/C(9) (*Table 2* and *Fig. 1*) have two H-atoms near the carbonyl O-atom at distance in the 2.03(6)–2.19(7)-Å range (2.23(3) Å in **5b**). Moreover, an intermolecular contact, 0.4 Å shorter than the sum of *van der Waals* radii [16] involving another H-atom of Me(16) is present in molecule B. In molecule A, a similar situation is found, but at 2.73(6) Å (*Table 3*).

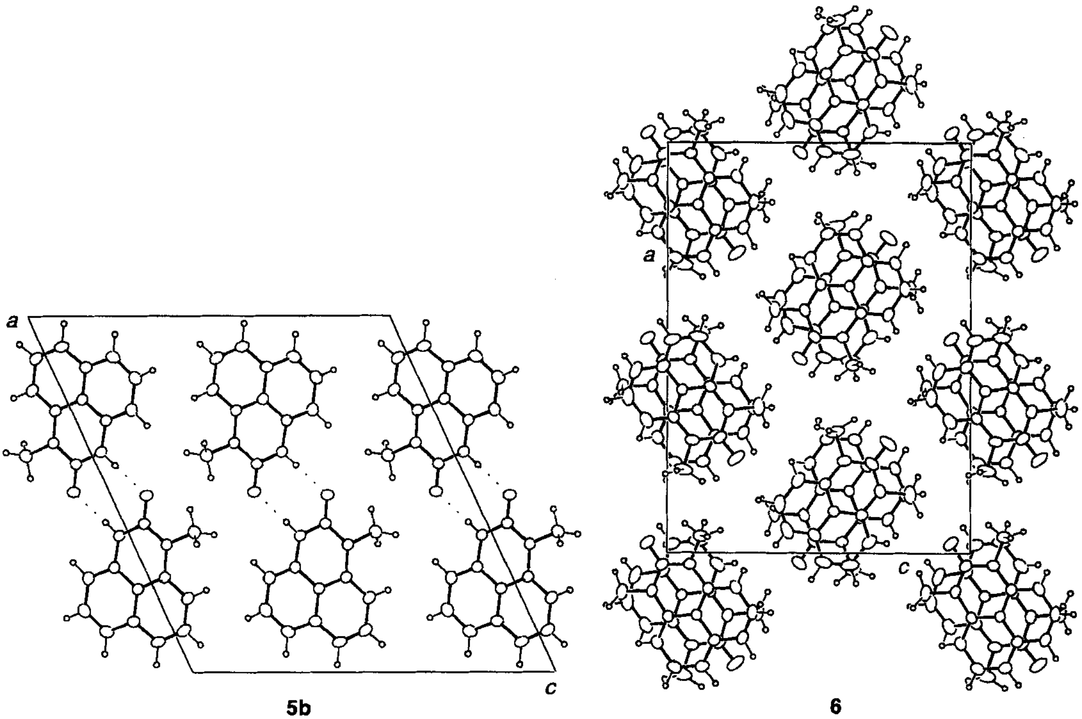
Compound **5b** forms H-bonded dimers through a crystallographic symmetry center (*Fig. 2*). Each molecule packs with itself, head to head, along the *b* axis with a mean distance of 3.455(1) Å, suggesting π interactions between them. A similar packing is observed in compound **6** (*Fig. 2*) although the stacking corresponds to piles of molecules A and B faced mutually head-to-tail. All distances involving the centroids of the aromatic rings are given in *Table 3*. The total packing coefficients are 0.72 and 0.71, respectively.

Similarly to the diarylureas [17], the elongation of the C=O bond and the shortening of the adjacent C(12)–N(13) bond in **5b** can be attributed to the strong H-bond present in this molecule (*Table 3*). In **6**, the elongation of the C=O distance could be due to the weak intra- and intermolecular C–H···O interactions. All C=O distances are similar to that reported by *Klebe* [18] for this group when it is involved in H-bond interactions (*i.e.* 1.237(25) Å *vs.* 1.215(15) Å, when the C=O is not involved in H-bonds). The opening of the intracyclic angle at N(13) could be assigned to the absence of the Me substituent.

Table 3. *Hydrogen Bonds and Aromatic Interactions*

	X–H	X···Y [Å]	H···Y [Å]	X–H···Y [°]	Symmetry
5b					
N(13)–H(13)...O(14)	0.86(3)	2.836(2)	1.97(3)	179(2)	$1-x, -y, -z$
C(15)–H(151)...O(14)	0.99(3)	2.709(3)	2.23(3)	108(2)	x, y, z
C(1–10)...C(5–10)[a])	–	3.606(1)	–	–	$x, -1+y, z$
C(5–10)...C(1–13)[a])	–	3.802(1)	–	–	$x, 1+y, z$
6					
C(15A)–H(152A)...O(14A)	0.95(6)	2.694(6)	2.16(6)	114(4)	x, y, z
C(16A)–H(163A)...O(14A)	0.96(7)	2.707(5)	2.19(7)	113(5)	x, y, z
C(15B)–H(151B)...O(14B)	1.10(6)	2.700(7)	2.03(6)	116(4)	x, y, z
C(16B)–H(161B)...O(14B)	0.92(8)	2.700(7)	2.17(8)	116(6)	x, y, z
C(16A)–H(162A)...O(14B)	1.03(4)	3.415(6)	2.39(4)	156(4)	$\frac{1}{2}-x, -\frac{1}{2}+y, -\frac{1}{2}+z$
C(16B)–H(162B)...O(14A)	1.15(6)	3.811(6)	2.73(6)	156(4)	$-x, 1-y, \frac{1}{2}+x$
C(1–10)A...C(1–13)B[a])	–	3.574(2)	–	–	$x, -1+y, z$
C(5–10)A...C(1–13)B[a])	–	3.604(2)	–	–	x, y, z
C(1–13)A...C(1–10)B[a])	–	3.476(2)	–	–	$x, -1+y, z$
C(1–13)A...C(5–10)B[a])	–	3.604(2)	–	–	x, y, z

[a]) C(1–10), C(5–10), and C(1–13) represent the centroids of the corresponding rings.



5b **6**

Fig. 2. *Crystal packing along the* b *axis evidencing the dimer molecules in* **5b** *and pair of alternating independent molecules in* **6**

To find out the influence of the substituents on the perimidinone geometry and to determine if the deformations observed in the naphthalene moiety are due to the crystal packing, several AM1 semiempirical calculations [19], starting from different geometries, were carried out for **5b** and **6**. All geometrical parameters, including those of the Me conformation, were optimized. These calculations revealed that *i*) the staggered conformation with respect to C(1)/C(9) is the most stable, *ii*) the three-ring system is planar, and *iii*) only small differences in the C–N distances (0.008 Å) and in the C(1)–C(10)–C(9) angle (1°) are observed as a consequence of the *N*-substitution.

^{13}C-NMR Spectroscopy: Solution and Solid-State Studies. The comparison of the chemical shifts of benzimidazole derivatives **13**, **14**, and **17** in solution leaves no doubt that the major tautomer of **13** is the oxo form 1-methyl-1*H*-benzimidazol-2(3*H*)-one

Table 4. *^{13}C-NMR Data in Solution and in Solid State* (CP/MAS) *of Benzimidazole Derivatives.* δ in ppm, *J* in Hz.

	Conditions	C(2)	C(3a)	C(4)	C(5)	C(6)	C(7)	C(7a)	Others
3	(D_6)DMSO [22]	155.5	129.8	108.7	120.5	120.5	108.7	129.8	–
	CP/MAS a)	159.0	128.8 c)	110.7	120.2 d)	121.3 d)	110.7	130.5 c)	–
	CP/MAS b)	158.3	129.1 c)	110.8	120.2 d)	121.5 d)	110.8	130.5 c)	–
13	(D_6)DMSO	154.5	128.2	108.6 (^1J = 163.8)	120.5 (^1J = 161.2) c)	120.8 (^1J = 161.7) c)	107.5 (^1J = 162.1)	131.0	26.3 (^1J = 139.4)
	CP/MAS a)	155.7	127.5	110.8	120.6 c)	123.0 c)	106.8	130.6, 132.5	24.0
	CP/MAS b)	156.2	127.7, 129.5	110.7	120.7 c)	122.8 c)	106.7	130.8, 133.3	24.4
14	(D_6)DMSO	153.7	129.6	107.4 (^1J = 162.9)	120.7 (^1J = 161.5, ^3J = 6.4, ^2J = 1.6)	120.7 (^1J = 161.5, ^3J = 6.4, ^2J = 1.6)	107.4 (^1J = 162.9)	129.6	26.8 (^1J = 139.7)
	CP/MAS a)	153.3(br.)	129.3	109.8	119.9 c)	121.2 c)	105.1	129.3	24.7
	CP/MAS b)	155.3, 153.6	130.9	111.5	121.5 c)	123.0 c)	106.7	130.9	28.2, 26.4
15	(D_6)DMSO	154.0	128.3	108.7 (^1J = 162.4)	120.5 (^1J = 161.0) c)	120.7 (^1J = 160.8) c)	107.5 (^1J = 163.3)	129.9	34.6 (^1J = 139.1, ^2J = 4.4), 13.4 (^1J = 127.0, ^2J = 2.9)
	CP/MAS a)	155.1	128.6	107.9	120.9	120.9	107.9	129.6	36.1, 11.8, 37.7
16	$CDCl_3$	158.5	141.0	117.7	121.4 c)	121.7 c)	109.4	132.1	56.9
	CP/MAS b)	161.8, 159.7	142.2	118.9	122.2 c)	123.6 c)	114.1	136.9, 135.5	55.9
17	$CDCl_3$	157.7	139.6	117.2 (^1J = 161.7)	120.5 (^1J = 160.2) c)	121.1 (^1J = 159.7) c)	107.6 (^1J = 159.7)	134.0	56.7 (^1J = 147.6), 27.5 (^1J = 139.9)
	CP/MAS b)	157.4	139.8	117.2	119.9 c)	122.5 c)	107.8, 105.8	134.0	58.6, 57.1, 26.1

a) Without Al_2O_3. b) With Al_2O_3. c) d) The assignment of these signals is arbitrary.

(*Table 4*). More sensitive and also more remote from the substituents than the C(2) atom are atoms C(3a) and C(4) which have chemical-shift differences of *ca.* 10 ppm depending on the tautomer. Compound **16** can also be used as a model for 1*H*-benzimidazol-2-ol (**3a**) since, even in CDCl$_3$, there is no annular tautomerism H–N(1)$\rightleftharpoons$H–N(3). This latter behavior is observed sometimes in benzimidazoles depending on the substituent at position 2 and on the solvent [20] [21]. Compounds **3** and **15** have spectra very similar to those of **13** and are thus also 1*H*-benzimidazol-2(3*H*)-ones.

In the solid state, the conclusion concerning tautomerism is the same as in solution, *i.e.* the most stable tautomers are the oxo forms **3b**, **13**, and **15**; however, in the solid state, only one tautomer is present whilst in solution the 1*H*-benzimidazol-2(3*H*)-ones are the most abundant tautomers. The CP/MAS (cross polarization/magic-angle spinning) ^{13}C-NMR spectra of **3** shows no splitted signals which is consistent with the X-ray structure [23] showing only one independent molecule in the unit cell. On the other hand, the chemical shifts of the atom pairs C(3a)/C(7a) and C(5)/C(6), respectively, are different, thus the symmetry of local molecules is C_s and not C_{2v}, an observation also consistent with the molecular structure determined by crystallography [23]. The structure of the remaining benzimidazoles was not determined, but the splitting of some ^{13}C-NMR signals (C(3a) and C(7a) in **13**; C(2) and Me–N in **14**; CH$_2$–N in **15**; C(2) and C(7a) in **16**, and C(7) and MeO in **17**) suggests that there are, at least, two independent molecules in the unit cell.

There are only preliminary accounts on the ^{13}C-NMR spectroscopy of perimidine derivatives in solution [5] [6]. Thus, we report in *Table 5* the chemical shifts and some coupling constants of some perimidine derivatives, including model compound **11**. It can be observed that the NH derivatives, perimidine and 2-chloroperimidine, show averaged signals for pairs of 'tautomeric' C-atoms, *e.g.* C(3a) and C(9a).

Table 5. *^{13}C-NMR Data of Perimidine*

	Solvent	C(2)	C(3a)	C(4)	C(5)	C(6)
1*H*-Perimidine (**1**)	CDCl$_3$	146.3 (^1J = 203.4)	140.9	108.4 (^1J = 161.1)	128.2 (^1J = 159.9)	120.8 (^1J = 163.3)
	(D$_6$) DMSO	146.5 (^1J = 199.4)	141.0	107.7 (^1J = 160.8, ^3J = 7.7)	128.4 (^1J = 158.3)	118.6 (^1J = 161.2, ^3J = 7.0, 4.2)
1-Methyl-1*H*-perimidine	CDCl$_3$	148.2 (^1J = 198.6, ^3J = 3.9)	143.0	114.6 (^1J = 162.7)	127.1 (^1J = 159.4)	119.9 (^1J = 163.1)
	(D$_6$) DMSO	149.2	143.8	114.1	127.8	119.4
2-Chloro-1*H*-perimidine	(D$_6$) DMSO	150.3	137.8 (^3J = 7.3)	104.3 (^1J = 160.0)	128.2 (^1J = 159.2)	117.8 (^1J = 163.2)
2-Chloro-1-methyl-1*H*-perimidine	(D$_6$) DMSO	149.9	138.7 (^3J = 6.9)	104.4 (^1J = 162.3, ^3J = 7.3)	128.0 (^1J = 159.0)	118.6 (^1J = 162.7)
11	CDCl$_3$	153.0	143.5	113.5	127.7	118.7
	(D$_6$) DMSO	152.7	143.4 (^3J = 8.6)	113.0 (^1J = 159.5, ^3J = 8.3, ^1J = 1.3)	127.6 (^1J = 159.2)	118.2 (^1J = 161.7, ^3J = 6.7, 4.5)

Table 6 summarizes the ^{13}C-NMR data for perimidinones in solution. Here again, the signals corresponding to atoms C(3a) and C(4) are the most useful for determining the tautomerism. In agreement with our previous conclusion [6], perimidinones exist as such in solution, *i.e.* the major tautomers are the oxo forms **2b**, **5b**, **7b**, **9b**, and **12**. Moreover, the chemical shifts of C(3a) and C(4) in pairs of benzimidazoles and perimidines carrying identical substituents in positions 1 and 2, are linearly related (**3**/**2**, **13**/**5**, **14**/**6**, **15**/**7**, **17**/**11**). δ(C(perimidine)) = $-51.2 + 1.44\,\delta$(C(benzimidazole)), $n = 5$, $r = 0.98$. This confirms that the tautomerism in both series (**3**/**2**, **13**/**5**, **15**/**7**) is similarly shifted towards the oxo tautomer.

The solid-state CP/MAS ^{13}C-NMR spectra are reported in *Table 7*. The data of **5** (no splitting) and **6** (split signals) are consistent with their X-ray crystal-structure data (see above) which indicate that for 1-methyl-1*H*-perimidin-2(3*H*)-one only one independent molecule **5b** (oxo form) exists in the unit cell, whilst for 1,3-dimethyl-1*H*-perimidin-2(3*H*)-one (**6**), there are two independent molecules. Although we were unable to obtain convenient crystals of perimidinone **2** (a rather unstable compound which darkened considerably in solution), the chemical shifts reported in *Table 7* show that like its 1-methyl derivative **5b**, it is present in its oxo form **2b**. Thus, 1*H*-perimidin-2(3*H*)-ones and 1*H*-benzimidazol-2(3*H*)-ones, both in solution and in the solid state, are oxo tautomers.

Gas-Phase Studies. In many cases, mass spectrometry (MS) was used to determine the structure of isolated tautomeric molecules in the gas phase [24]. In this work, we used tandem MS methods to determine the true structure of perimidinone **2**. The electron-impact (EI) MS (70 eV; *Table 8*) of **2** is characterized by an intense signal at m/z 166 arising from loss of H_2O from the molecular ion $M^{+\cdot}$ (m/z 184). This reaction is the only one

Derivatives in Solution. δ in ppm, J in Hz.

C(6a)	C(7)	C(8)	C(9)	C(9a)	C(9b)	Others	
135.3	120.8 $(^1J = 163.3)$	128.2 $(^1J = 159.9)$	108.4 $(^1J = 161.1)$	140.9	122.9	–	
135.4	118.6 $(^1J = 161.2,$ $^3J = 7.0, 4.2)$	128.4 $(^1J = 158.3)$	107.7 $(^1J = 160.8,$ $^3J = 7.7)$	141.0	123.0	–	
134.9	119.2 $(^1J = 161.4)$	128.4 $(^1J = 159.6,$ $^5J = 2.8)$	100.1 $(^1J = 160.5)$	138.0	122.4	35.5 $(^1J = 139.4,$ $^3J = 2.8)$	
134.9	118.6	128.6	100.5	138.5	122.2	35.6	
134.3	117.8 $(^1J = 163.2)$	128.2 $(^1J = 159.2)$	104.3 $(^1J = 160.0)$	137.8 $(^3J = 7.3)$	113.9	–	
134.0	117.8 $(^1J = 163.6)$	128.1 $(^1J = 159.9)$	104.0 $(^1J = 162.1)$	136.4 $(^3J = 7.9)$	113.9 $(^3J = 8.0)$	29.1 $(^1J = 139.8)$	
135.0	118.5	128.7	100.8	140.4	120.3	54.6	30.3
134.6	118.0 $(^1J = 161.3,$ $^3J = 7.2, 3.8)$	128.6 $(^1J = 157.7)$	101.5 $(^1J = 161.8,$ $^3J = 7.3, ^2J = 1.6)$	140.0	119.8	54.7 $(^1J = 147.7)$	30.3 $(^1J = 140.7)$

Table 6. *^{13}C-NMR Data of 1*H*-Perimidin-2(3*H*)-one Derivatives in Solution.* δ in ppm, J in Hz.

	Solvent	C(2)	C(3a)	C(4)	C/5)	C(6)	C(6a)	C(7)	C(8)	C(9)	C(9a)	C(9b)	Others
2	(D$_6$)DMSO	150.0	135.6	103.8	127.8	117.6	134.0	117.6	127.8	103.8	135.6	113.6	–
5	CDCl$_3$	151.4	135.5	104.6 (^1J = 159.2)^a)	127.8 (^1J = 159.9)	118.9 (^1J = 161.9, ^3J = 7.0, 4.4)	134.4	119.5 (^1J = 162.1, ^3J = 6.8, 3.9)	127.8 (^1J = 159.9)	104.2 (^1J = 161.4) ^3J = 7.1, ^2J = 2.6)	138.5	114.7	29.5 (^1J = 139.8)
	(D$_6$)DMSO	149.8	136.5	104.2 (^1J = 162.7)^a)	127.9 (^1J = 159.5)	117.7 (^1J = 162.2, ^3J = 7.0, 4.3)	133.9	118.5 (^1J = 162.6, ^3J = 6.6, 4.5)	128.0 (^1J = 159.7)	103.9 (^1J = 161.7)^a)	138.6	113.8	28.9 (^1J = 139.7)
6	CDCl$_3$	150.8	137.6	103.8 (^1J = 162.2. ^3J = 7.6, ^2J = 2.3)	127.6 (^1J = 159.7)	119.1 (^1J = 161.2, ^3J = 6.9, 4.4)	134.1	119.1 (^1J = 162.2, ^3J = 6.9, 4.4)	127.6 (^1J = 159.7)	103.8 (^1J = 162.2, ^3J = 7.6, ^2J = 2.3)	137.6	114.6	30.5 (^1J = 139.8)
	(D$_6$)DMSO	149.9	137.3	104.3	128.0	118.7	133.6	118.7	128.0	104.3	137.3	113.7	30.4
7	(D$_6$)DMSO	149.6	136.4	104.0 (^1J = 161.5, ^3J = 8.2)	127.9 (^1J = 159.6)	117.8 (^1J = 162.3, ^3J = 7.0, 4.4)	134.3	118.4 (^1J = 162.7, ^3J = 6.5, 4.4)	128.1 (^1J = 159.8)	103.7 (^1J = 161.2, ^3J = 8.0, ^2J = 2.3)	137.3	114.2	36.4 (^1J = 139.6, ^2J = 4.3), 11.2 (^1J = 126.9, ^2J = 2.9)
8	(D$_6$)DMSO	149.3	136.2	103.9 (^1J = 161.0, ^3J = 8.1, ^2J = 2.4)	128.0 (^1J = 160.1)	118.6 (^1J = 162.8, ^3J = 6.8, 4.5)	134.4	118.6 (^1J = 162.8, ^3J = 6.8, 4.5)	128.0 (^1J = 160.1)	103.9 (^1J = 161.0, ^3J = 8.1, ^2J = 2.4)	136.2	114.5	37.7 (^1J = 140.0, ^2J = 4.2) 11.2 (^1J = 127.0, ^2J = 3.1)
9	(D$_6$)DMSO	149.9	137.6	104.1 (^1J = 161.3)	127.9 (^1J = 159.6)	117.8 (^1J = 162.3, ^3J = 7.0, 4.5)	134.3	118.4 (^1J = 162.7, ^3J = 6.6, 4.6)	128.0 (^1J = 159.8)	103.9 (^1J = 161.2)	136.4	114.2	42.9 (^1J = 138.9), 18.9 (^1J = 138.9), 11.0 (^1J = 124.9)

10	(D$_6$)DMSO	149.8	136.4	104.1 (^1J = 162.8, ^3J = 7.8) ^2J = 2.2)	127.8 (^1J = 160.2)	118.6 (^1J = 162.8, ^3J = 6.5, 4.6)	134.3	118.6 (^1J = 162.8, ^3J = 6.5, 4.6)	127.8 (^1J = 160.2)	104.1 (^1J = 161.2, ^3J = 7.8, ^2J = 2.2)	136.4	114.4	44.1 (^1J = 139.1), 18.7 (^1J = 125.9), 11.0 (^1J = 125.4)
12	(D$_6$)DMSO	149.2	134.6	106.0 (^1J = 161.8)	127.4 (^1J = 161.8)	119.2 (^1J = 163.0, ^3J = 7.0, 4.2)	133.9	121.3 (^1J = 164.1)	127.6 (^1J = 160.9)	109.1 (^1J = 161.7, ^3J = 8.0, ^2J = 2.3)	133.8	113.9	175.3 (CO), 38.7 ^1J = 130.8

[a]) The assignment of these signals is arbitrary.

Table 7. *CP/MAS ^{13}C-NMR Data of 1*H*-Perimidin-2-(3*H*)-one Derivatives in the Solid State.* δ in ppm.

	C(2)	C(3a), C(9a)	C(4), C(9)	C(5), C(8)	C(6), C(7)	C(6a)	C(9b)	Others
2[a])	157.1, 152.0	136.5	104.5	127.8	118.6	135.1, 133.9	114.8	–
2[b])	155.5 (br.)	134.7	104.9	128.1	119.1	134.7	115.0	–
5[b])	153.2	137.4, 139.3	102.5, 103.6	125.9, 127.4	118.8, 118.8	134.5	114.2	30.7
6[b])	149.5, 147.5	139.2, 137.3	104.7	127.4	118.9	133.8	114.3	30.1
7[b])	150.8	136.8	104.6	126.9, 128.4	115.9	134.7	119.2	34.7, 11.9
8[b])	150.1	136.1	104.2	128.2	119.9, 121.0	136.1	115.5	39.4, 38.2, 11.9
11[b])	151.6	139.9, 144.2	101.8, 115.6	126.6, 130.0	118.5, 118.5	134.6	118.5	55.5, 29.1, 27.6
1-Methyl-1*H*-perimidine[a])	150.0	138.4, 143.7	102.0, 114.5	129.2, 129.2	117.8, 119.2	135.0	123.1	35.1

[a]) Without Al_2O_3. [b]) With Al_2O_3.

Table 8. *Selected Peaks in the 70-eV Electron-Impact Mass Spectra of* **2**, **12**, *and* **9**

	m/z							
	226	197	184	166	156	155	140	139
Perimidinone **2**	–	–	*100*	70	16	20	11	16
1-Acetylperimidinone **12**	15	–	*100*	49	14	14	7	10
1-Propylperimidinone **9**	*100*	48	87	32	8	8	10	5

observed from metastable peaks, the kinetic energy liberated during this process ($T^{50}_{H_2O}$) amounts to 54 meV. This H_2O loss involves specifically both acidic H-atoms, *i.e.* the N–H's, since (1,3-D_2)-**2** eliminates only D_2O. Activation by collision of $M^{+\cdot}$ of **2** leads to the CA (Collision Activation)-MS of *Fig. 3*. An interesting reaction is that yielding *m/z* 140 since it involves the loss of C, H_2, N, and O from $M^{+\cdot}$.

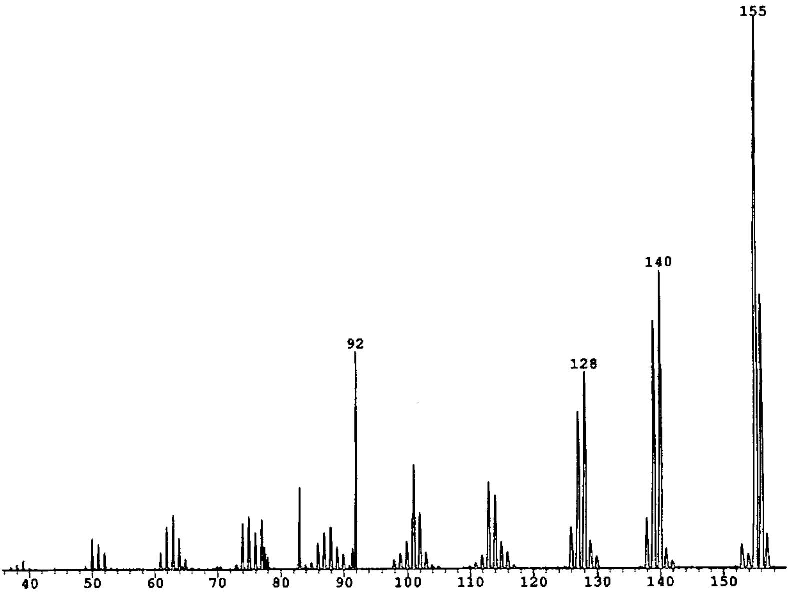
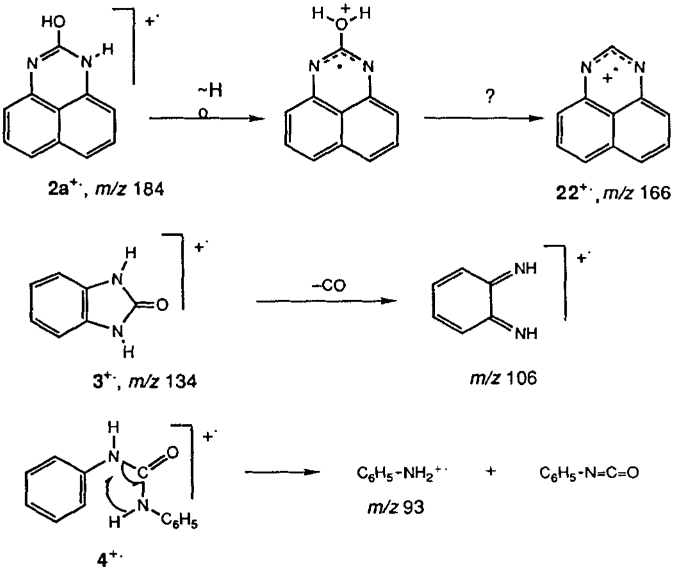


Fig. 3. *CA-MS of perimidinone* **2**

The EI-MS of perimidinone **2** is in total contrast with that of the model molecules benzimidazolone **3** and diphenylurea **4**. For **3**, the only observed process is a decarbonylation (*m/z* 134→106) leading to ions which may have a structure of *o*-benzoquinone diimine (*Scheme 2*). For urea **4**, the less-demanding energetic reaction corresponds to the elimination of phenyl isocyanate to form ionized aniline (*Scheme 2*). The formation of $[C_6H_5N{=}C{=}O]^{+\cdot}$ is observed only for high internal energy (MS and CA-MS of $M^{+\cdot}$). This different behavior suggests that molecular ion $\mathbf{2}^{+\cdot}$ exists in the hydroxy form $\mathbf{2a}^{+\cdot}$. The H_2O loss could occur through a [1,3]-H transfer (from N to O) which is energy costly (*ca.* 43 kcal mol^{-1} [25]). On the other hand, AM1 calculations [19] [26] show that $\mathbf{2b}^{+\cdot}$ ions are more stable than $\mathbf{2a}^{+\cdot}$ ions by 5.0 kcal mol^{-1} (193.5 and 198.5 kcal mol^{-1}, resp.). In conclusion, the sequence $\mathbf{2b}^{+\cdot} \rightarrow \mathbf{2a}^{+\cdot} \rightarrow [\mathbf{2a} - H_2O]^{+\cdot}$ has been definitely established.

To explore if the hydroxy form $\mathbf{2a}^{+\cdot}$ can be generated *in situ* we analyzed the MS of 1-propylperimidinone **9** and 1-acetylperimidinone **12** which can lose propene and ketene, respectively. These fragmentations are actually observed (*Table 8*). The CA-MS of the ions $[M - C_3H_6]^{+\cdot}$ (from **9**) and $[M - C_2H_2O]^{+\cdot}$ (from **12**) are identical to the CA-MS of $\mathbf{2}^{+\cdot}$. Since the calculated barrier between $\mathbf{2a}^{+\cdot}$ and $\mathbf{2b}^{+\cdot}$ is very high, this spectral identity points to a common ionic structure. An independent confirmation for such a common structure is provided by the value of the $T^{50}_{H_2O}$ term which is 55 meV for the dehydration

Scheme 2



of $[M - C_3H_6]^{+\cdot}$ (from **9**) and 52 meV for the dehydration of $[M - C_2H_2O]^{+\cdot}$ (from **12**).

As expected, the CA-MS of the fragments m/z 166 obtained from **2**, **9**, and **12** are identical and dominated by a loss of CHN (*Fig. 4a*). A characteristic of these spectra is the great abundance of doubly charged ions (m/z 83). In neutralization/reionization experiments (*Fig. 4b*), a recovery signal (RS) of weak intensity if observed. Even if the formation of a 'ionized carbodiimide' $\mathbf{22}^{+\cdot}$ cannot be excluded, the experimental results are insufficient to prove it.

In flash pyrolysis under vacuum at 700°, perimidinone **2** is stable and no H_2O elimination is observed. Consequently, the behavior of **2** in the MS experiment is completely different from that of the neutral molecule in flash vacuum pyrolysis.

Calculations. To discuss the equilibria **2a**$\rightleftharpoons$**2b** and **3a**$\rightleftharpoons$**3b**, we carried out AM1 semi-empirical calculations on both systems. Thus, the calculated heats of formation are 28.1 kcal mol^{-1} for **2a**, 14.8 kcal mol^{-1} for **2b**, 27.0 kcal mol^{-1} for **3a**, and 13.7 kcal mol^{-1} for **3b**. The corresponding differences in energy are 13.3 kcal mol^{-1} for **2a**/**2b** and 13.2 kcal mol^{-1} for **3a**/**3b**. All geometries were fully optimized; for **2a**, **2b**, and **3a**, the resulting geometries correspond to planar structures but for benzimidazolone **3b**, the calculated structure has the H-atoms at N(1) and N(3) out-of-plane.

Not only 1*H*-benzimidazol-2(3*H*)-one itself (ZEFXIR) but most *C*- and *N*-monosubstituted derivatives found in the *Cambridge Structural Database* [27a] are in the oxo form; the only exception is kealiiquinone (= 6,7-dimethoxy-4-(4-methoxyphenyl)-1-methyl-1*H*-naphth[2,3-*d*]imidazole-2,5,8(3*H*)-trione; VEHBUF) which exists in the crystal with a 1-methyl-1*H*-benzimidazol-2-ol moiety. The authors report, although without discussion, the ^{13}C-NMR chemical shifts of kealiiquinone [27b]; a comparison

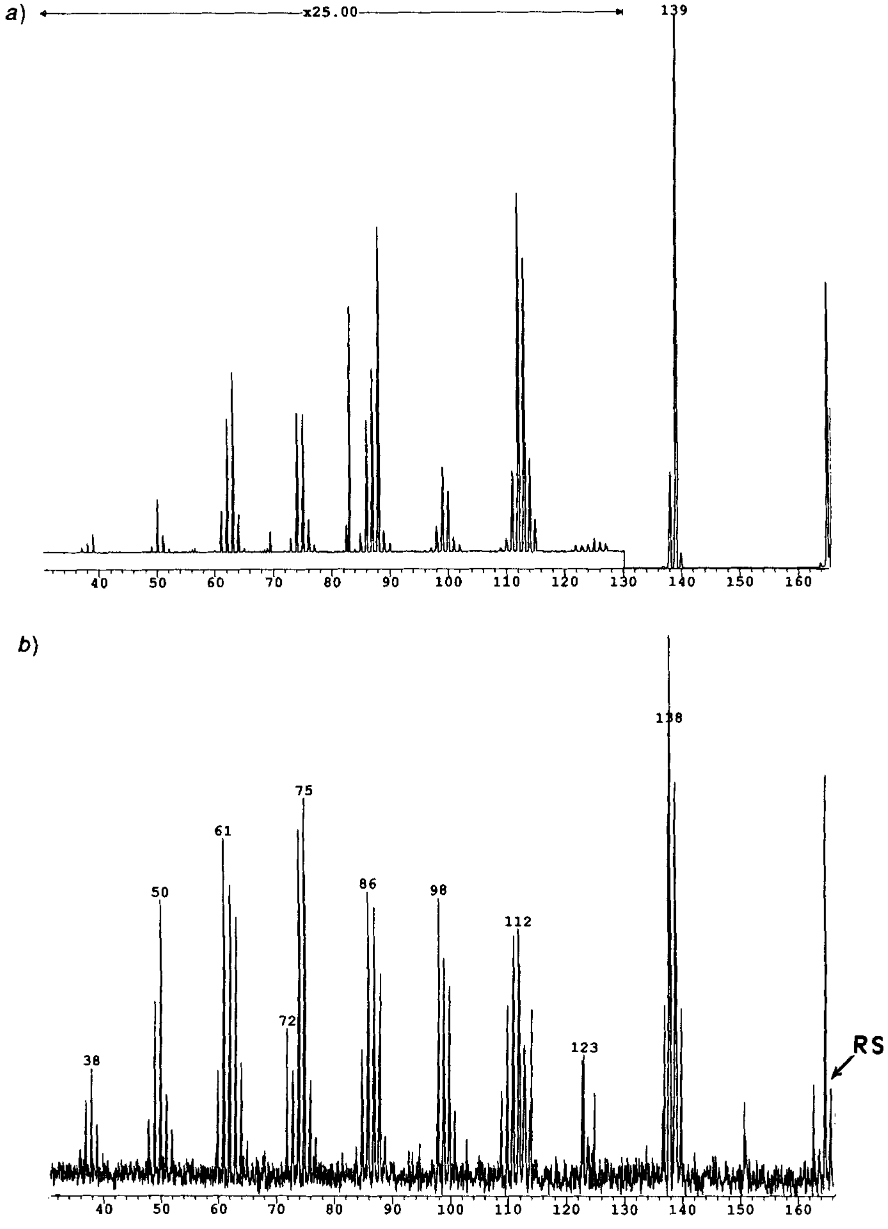


Fig. 4. a) *CA-MS of fragment* m/z *166 and* b) *neutralization/reionization spectrum.* RS = recovery signal.

with the data of *Table 4* shows that kealiiquinone should exist in the hydroxy form, even in DMSO solution, a rather surprising result.

Afterwards, we obliged benzimidazolone **3b** to be planar, and the resulting heat of formation was 13.9 kcal mol^{-1} (only 0.1 kcal mol^{-1} higher than the minimum). Consequently, the equilibria **2a** $\rightleftarrows$ **2b** and **3a** $\rightleftarrows$ **3b** are very similar according to AM1 calculations. If we assume, according to *Cook et al.* [28], that perimidines have little aromatic character in the heteroring, then the fact that the differences in energy are almost the same (13 kcal mol^{-1}) should correspond to perimidinone being much less stable than benzimidazolone.

3. Conclusions. –There is a complete parallelism between 1*H*-perimidin-2(3*H*)-one (**2**) and 1*H*-benzimidazol-2(3*H*)-one (**3**) in solution (predominance of the oxo tautomer) and in the solid state (existence of the oxo tautomer). In the gas phase, although the oxo tautomers remain the most stable in the ground state, ionization reduces the energy gap in the case of **2** (from 13.3 to 5.0 kcal mol^{-1} according to AM1 calculations) and the loss of H_2O is observed from the hydroxy tautomer, while **3** loses CO from the oxo tautomer.

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Experimental Part

General. Naphthalene-1,8-diamine, 1*H*-benzimidazol-2(3*H*)-one (**3**), 1-methyl-1*H*-benzimidazol-2(3*H*)-one (**13**), 1-ethyl-1*H*-benzimidazol-2(3*H*)-one (**15**), and 1,3-diphenylurea (**4**) are commercial products and were used without further purification. The following compounds were prepared according to published procedures: 1,3-dimethyl-1*H*-benzimidazol-2(3*H*)-one (**14**) [9], 2-methoxy-1-methyl-1*H*-benzimidazole (**17**) [10], 1*H*-perimidine (**1**) [29], 12-methyl-1*H*-perimidine [29], 1*H*-perimidin-2(3*H*)-one (**2**) [7], 1-methyl-1*H*-permidin-2(3*H*)-one (**5**) [7], 1,3-dimethyl-1*H*-perimidin-2(3*H*)-one (**6**) [8], 1,3-diethyl-1*H*-perimidin-2(3*H*)-one (**8**) [8] and 1,3-dipropylperimidin-2(3*H*)-one (**10**) [8]. Flash Vacuum Pyrolsis: the pyrolysis system using a quartz tube 50-mm long and 3-mm wide was described elsewhere [30]. M.p.: hot-stage microscope; uncorrected. ^{1}H- and ^{13}C-NMR Spectra (solutions): see *Tables 9* and *10* and *Tables 4–6*, resp.; *Bruker-AC-200* instrument at 200.14 and 50.32 MHz, reps.; chemical shifts (δ) in ppm rel. to internal Me_4Si (= 0 ppm) accuracy 0.01 ppm for ^{1}H and 0.1 ppm for ^{13}C; coupling constants *J* in Hz, accurate to ±0.2 and ±0.6 Hz, resp. ^{13}C-NMR Spectra (solid-state): *Tables 4* and *7*; with pure solids and solids adsorbed on alumina *Merck 90* for chromatography (70–230 mesh ASTM, No. 1077), ratio 1:4 to 1:8 (*w*/*w*) for org. and inorg. solids [31]; *Bruker-AC-200* spectrometer at 50.32 MHz under conditions of CP (cross polarization) and MAS (magic-angle spinning), using a 7-mm *Bruker DAB 7* probehead which achieves rotation frequencies of *ca.* 3.5–4.5 kHz; standard CP/MAS pulse sequence with 7 µs ^{1}H-90° pulse width, 3–5 ms contact pulses, and 5 s repetition time, spectral width 20000 Hz; chemical shifts rel. to the spectrometer references frequency which was calibrated by the glycine signal at 176.1 ppm. Mass Spectra (EI, 70 eV): six-sectors *VG-AutoSpec-6F* mass spectrometer with an $E_1B_1E_2E_3B_2E_4$ (E electric sector, B magnetic sector) geometry working at 8 kV [32]; in CA experiments, an ion beam was mass-selected by a combination of the first three sectors ($E_1B_1E_2$) and subjected to collision in an O_2-pressurized cell (80% transmission); in neutralization/reionization experiments, neutralization of ions by NH_3 (80% transmission) occurred before reionization by O_2, residual ions were eliminated by floating at 9 kV the intermediate calibration source situated between both cells; both kind of spectra were recorded sweeping in a synchronous way the $E_3B_2E_4$ fields.

X-Ray Crystal-Structure Determination. X-Ray data and experimental details for compounds **5b** and **6** are given in *Table 11*. The structures were solved by direct methods [33], the non-H-atoms were refined anisotropically and the H-atoms included as isotropic. In **6**, 7 reflections were affected by secondary extinction and were considered as unobserved in the last cycles of refinement. Most of the calculations were performed on a *VAX6410* computer using the XRAY80 system [34]. The atomic scattering factors were taken from [35]. The two independent molecules in compound **6** are related through a pseudosymmetry [36] center located at (0.12, 0.33, 0.55). The matching of the independent molecules resulted in a χ^2 value lower than the tabulated one, 1.88, 4.58, 1.34 *vs.* 21.00 (95%) for the *x*, *y*, and *z* coordinates, resp. Attempts to solve and refine the structure (taken into account the previous relationship) in the *Pnam* centrosymmetric space group were unsuccessful. Fractional atomic coordinates, thermal factors for the non-H-atoms, H-parameters, bond lengths and angles, and tables of structure factors were deposited with the *Cambridge Crystallographic Data Center*.

Table 9. *^{1}H-NMR Data of Perimidine Derivatives in Solution.* δ in ppm, *J* in Hz.

	Solvent	H–C(2)	H–C(4)	H–C(5)	H–C(6)	H–C(7)	H–C(8)	H–C(9)	NH	Others	*J*
1	(D$_6$)DMSO	7.30 (*s*)	6.37 (*dd*)	7.08 (*dd*)	6.97 (*dd*)	6.97(*dd*)	7.08 (*dd*)	6.37 (*dd*)	10.54	–	*J*(4,5) = 7.2, *J*(5,6) = 8.3, *J*(7,8) = 8.3, *J*(8,9) = 7.2, *J*(4,6) = 1.1, *J*(7,9) = 1.1
1-Methyl-1*H*-perimidine	CDCl$_3$	7.24 (*s*)	6.84 (*dd*)		7.10–7.30 (*m*)			6.10 (*m*)	–	3.12 (*s*)	*J*(4,5) = 7.1, *J*(4,6) = 1.4
	(D$_6$)DMSO	7.46 (*s*)	6.67 (*d*)		7.04–7.24 (*m*)			6.16 (*dd*)	–	3.09 (*s*)	*J*(4,5) = 6.9, *J*(8,9) = 6.9, *J*(7,9) = 0.8
2-Chloro-1*H*-perimidine	(D$_6$)DMSO	–	6.50 (*d*)		7.09–7.19 (*m*)			6.50 (*d*)	8.20	–	*J*(4,5) = 6.1, *J*(8,9) = 6.1
2-Chloro-1-methyl-1*H*-perimidine	(D$_6$)DMSO	–	6.57 (*m*)		7.12–7.33 (*m*)			6.57 (*m*)	–	3.20 (*s*)	
11	CDCl$_3$	–	6.80 (*dd*)		7.11–7.31 (*m*)			6.26 (*dd*)	–	3.22 (*s*), 3.98 (*s*)	*J*(4,5) = 7.3, *J*(8,9) = 6.7, *J*(4,6) = 1.2, *J*(7,9) = 1.8
	(D$_6$)DMSO	–	6.65 (*d*)		7.08–7.26 (*m*)			6.40 (*m*)	–	3.16 (*s*), 3.89 (*s*)	*J*(4,5) = 7.2, *J*(8,9) = 7.3

Table 10. *^{1}H-NMR Data of 1*H*-Perimidin-2(3*H*)-one Derivatives in Solution.* δ in ppm, *J* in Hz.

	Solvent	H–C(4)	H–C(5)	H–C(6)	H–C(7)	H–C(8)	H–C(9)	NH	Others	*J*
2	(D$_6$)DMSO	6.49	7.20	7.08	7.08	7.20	6.49	10.01	–	*J*(4,5) = 7.2, *J*(4,6) = 1.0, *J*(5,6) = 8.3, *J*(7,8) = 8.3, *J*(7,9) = 1.0, *J*(8,9) = 7.2
5	CDCl$_3$	6.55	7.31	7.23	7.26	7.34	6.55	8.30	3.39	*J*(4,5) = 6.6, *J*(4,6) = 1.9, *J*(5,6) = 8.3, *J*(7,8) = 8.3, *J*(7,9) = 1.3, *J*(8,9) = 7.2
	(D$_6$)DMSO	6.59	7.27	7.18	7.22	7.33	6.59	10.42	3.31	*J*(4,5) = 7.2, *J*(4,6) = 1.3, *J*(5,6) = 8.3, *J*(7,8) = 8.3, *J*(7,9) = 1.0, *J*(8,9) = 7.4
6	CDCl$_3$	6.56	7.37	7.28	7.28	7.37	6.56	–	3.44	*J*(4,5) = 7.3, *J*(4,6) = 1.2, *J*(5,6) = 8.3, *J*(7,8) = 8.3, *J*(7,9) = 1.2, *J*(8,9) = 7.3
7	(D$_6$)DMSO	6.46	7.15	7.05	7.09	7.22	6.57	10.40	3.91, 1.16	*J*(4,5) = 7.1, *J*(4,6) = 1.3, *J*(5,6) = 8.2, *J*(7,8) = 8.2, *J*(7,9) = 0.9, *J*(8,9) = 7.5
8	CDCl$_3$	6.51	7.25	7.16	7.16	7.25	6.51	–	3.99, 1.25	*J*(4,5) = 7.5, *J*(4,6) = 1.1, *J*(5,6) = 8.3, *J*(7,8) = 8.3, *J*(7,9) = 1.1, *J*(8,9) = 7.5
	(D$_6$)DMSO	6.74	7.36	7.26	7.26	7.36	6.74	–	3.98, 1.18	*J*(4,5) = 7.4, *J*(5,6) = 8.1, *J*(7,8) = 8.1, *J*(8,9) = 7.4
9	(D$_6$)DMSO	6.56	7.24	7.15	7.19	7.31	6.65	10.36	3.82, 1.62, 0.92	*J*(4,5) = 7.2, *J*(4,6) = 1.3, *J*(5,6) = 8.3, *J*(7,8) = 8.3, *J*(7,9) = 0.9, *J*(8,9) = 7.5
10	(D$_6$)DMSO	6.70	7.35	7.25	7.25	7.35	6.70	–	3.88, 1.62, 0.92	*J*(4,5) = 7.4, *J*(4,6) = 1.1, *J*(5,6) = 8.3, *J*(7,8) = 8.3, *J*(7,9) = 1.1, *J*(8,9) = 7.4
12	(D$_6$)DMSO	6.70 (*m*)		7.30–7.38			6.70 (*m*)	10.80	3.31	

Table 11. *X-Ray Crystal-Structure Analysis at Room Temperature*

	5b	**6**
Crystal data		
Formula	$C_{12}H_{10}N_2O$	$C_{13}H_{12}N_2O$
Crystal habit	colorless prism	colorless prism
Crystal size [mm]	0.43 × 0.20 × 0.07	0.57 × 0.20 × 0.20
Symmetry	monoclinic, $P2_1/c$	orthorombic, $Pna2_1$
Unit cell determination	least-squares fit from 43 reflexions ($\theta < 45°$)	least-squares fit from 56 reflexions ($\theta < 45°$)
Unit cell dimensions	a = 16.6965(15) Å	a = 18.9792(9) Å
	b = 4.0160(2) Å	b = 7.7580(3) Å
	c = 15.2874(14) Å	c = 13.8877(7) Å
	90°, 114.617(6)°, 90°	90°, 90°, 90°
Packing: V[Å^3], Z	931.9(1), 4	2044.8(2), 8
D_c [g/cm^3], M, F(000)	1.413, 198.22, 416	1.379, 212.25, 896
μ[cm^{-1}]	7.05	6.76
Experimental data		
Technique	four-circle diffractometer *Philips PW1100*, bisecting geometry, graphite-oriented monochromator, CuK_α, $\omega/2\theta$ scans, scan width 1.4°, detector apertures 1 × 1°, θ_{max} = 65°, 1 min/reflex.	
Number of reflexions:		
independent	1575	1820
observed	1344 ($3\sigma(I)$ criterion)	1702[a]) ($3\sigma(I)$ criterion)
Standard reflexions	2 reflexions every 90 min, No. of variation	
Solution	direct methods: SIR88	
Refinement least-squares on F_o	full matrix	
Number of variables	176	384
Degrees of freedom	1168	1318
Ratio of freedom	7.6	4.4
H-Atoms	from difference synthesis	
Weighting scheme	empirical as to give no trends in $\langle \omega \Delta^2 F \rangle$ *vs.* $\langle \lvert F_{obs} \rvert \rangle$ and $\langle \sin \theta/\lambda \rangle$	
Max. thermal value [Å^2]	U_{22}(O(14)) = 0.0836(9)	U_{33}(C(15B)) = 0.135(4)
Final ΔF peaks [eÅ^{-3}]	0.14	0.28
Final R and R_w	0.042, 0.053	0.056, 0.052

[a]) See *Exper. Part.*

*1-Ethyl-1*H*-perimidin-2(3*H*)-one* (**7**). To 1*H*-perimidin-2(3*H*)-one (**2**; 1 g, 5.43 mmol), finely powdered KOH (0.45 g, 8.1 mmol), and K_2CO_3 (7.5 g, 54.3 mmol) in acetone (40 ml), EtI (1.26 g, 8.1 mmol) was added and the mixture vigorously stirred and refluxed for 4 h. Then the mixture was filtered, the solvent distilled off, and the residue subjected to column chromatography (CC; silica gel, $CHCl_3$/AcOEt 9:1): **8** (0.31 g, 48%; R_f 0.60; m.p. 139–141° ([8]: 131–140°)), followed by pure **7** (0.29 g, 50%). R_f 0.27. M.p. 220–221° (from EtOH). Anal. calc. for $C_{13}H_{12}N_2O$ (212.26): C 73.56, H 5.70, N 13.20; found: C 73.31, H 5.82, N 13.26.

*1-Propyl-1*H*-perimidin-2(3*H*)-one* (**9**). As described for **7**, with **2** (1 g, 5.43 mmol), KOH (0.45 g, 8.1 mmol), K_2CO_3 (7.5 g, 54.3 mmol), acetone (40 ml), and propyl iodide (1.37 g, 8.1 mmol). **10** (0.36 g, 50%; R_f 0.64; m.p. 120–122° ([8]: 112–113°)) and pure **9** (0.27 g, 44%). R_f 0.27. M.p. 198–199°. Anal. calc. for $C_{14}H_{14}N_2O$ (226.29): C 74.31, H 6.24, N 12.38; found: C 74.79, H 6.14, N 12.65.

*2-Methoxy-1-methyl-1*H*-perimidine* (**11**). To a soln. of 2-chloro-1-methyl-1*H*-perimidine [7] (0.4 g, 1.89 mmol) in dry MeOH (6 ml), Na (0.43 g, 18.9 mmol) in anh. MeOH (4 ml) was added. The mixture was stirred for 12 h at r.t., the solvent evaporated, and the residue treated with H_2O and extracted with $CHCl_3$. CC ($CHCl_3$) gave **11** (92 mg, 23%). White solid. M.p. 113–114°. Anal. calc. for $C_{13}H_{12}N_2O$ (212.26): C 73.56, H 5.70, N 13.20; found: C 73.50, H 5.62, N 13.32.

*1-Acetyl-1*H*-perimidin-2(3*H*)-one* (**12**). As described for **7**, with **2** (1 g, 5.43 mmol), KOH (0.3 g, 5.43 mmol), anh. K_2CO_3 (7.5 g, 54.3 mmol), acetone (40 ml), and acetyl chloride (0.36 ml, 5.43 mmol): **12** (0.16 g, 13%). R_f 0.32. M.p. 177–179°. Anal. calc. for $C_{13}H_{10}N_2O_2$ (226.24): C 69.02, H 4.46, N 12.38; found: C 68.94, H 4.42, N 12.51.

*2-Methoxy-1*H*-benzimidazole* (**16**). M.p. 203–204° (toluene) ([11]: m.p. 198–200°). ^{1}H-NMR ($CDCl_3$): 8.53 (*s*, NH); 7.53–7.57 (*m*, 1 arom. H); 7.07–7.25 (*m*, 3 arom. H); 4.17 (*s*, MeO).

*1-Isopropenyl-1*H*-benzimidazol-2(3*H*)-one* (**18**). M.p. 119–121° ([37]: 121–122°). R_f (AcOEt/EtOH 9:1) 0.28. ^{1}H-NMR ($CDCl_3$): 7.06–7.17 (*m*, 4 arom. H); 10.39 (*s*, NH); 5.41, 5.25 (H_{cis} and H_{trans} of CH_2=); 2.25 ($J(Me,H_{cis}) = 1.2$, $J(Me,H_{trans}) = 0.6$, Me). ^{13}C-NMR ($CDCl_3$): 154.8 (CO); 128.4 (C(3a)); 109.9 ($^1J = 163.2$, C(4)); 121.2 ($^1J = 162.0$, $^3J = 7.2$, C(5)); 121.8 ($^1J = 161.6$, $^3J = 6.5$, $^2J = 1.7$, C(6)); 108.9 ($^1J = 163.2$, C(7)); 129.8 (C(7a)); 137.7 (Me*C*=CH_2); 113.9 ($^1J = 159.6$, $^3J = 4.9$, MeC=*C*H_2); 20.2 ($^1J = 128.5$, $^3J = 8.9$, $^3J = 4.3$, *Me*C=CH_2).

*2-Chloro-1-isopropenyl-1*H*-benzimidazole* (**19**). Oil ([32]: b.p. 95°/0.4 Torr). R_f (AcOEt/EtOH 9:1) 0.28. ^{1}H-NMR ($CDCl_3$): 6.88–7.75 (*m*, 4 arom. H); 5.60, 5.31 (H_{cis} and H_{trans} of CH_2=); 2.21 (*d*, $J(Me,H_{cis}) = 1.4$, Me). ^{13}C-NMR ($CDCl_3$): 140.2 (C(2)); 138.7 (C(3a)); 118.6 ($^1J = 163.5$, C(4)); 123.7 ($^1J = 161.8$, $^3J = 7.9$, C(5)); 123.2 ($^1J = 162.4$, C(6)); 110.1 ($^1J = 164.6$, C(7)); 134.6 (C(7a)); 137.4 (Me*C*=CH_2); 117.7 ($^1J = 160.6$, $^3J = 4.9$, MeC=CH_2); 20.9 ($^1J = 128.9$, $^3J = 8.7$, 4.1, *Me*C=CH_2).

*1-Isopropenyl-2-methoxy-1*H*-benzimidazole* (**20**). Oil. B.p. 102–104°/1.5 Torr ([11]: b.p. 102–104°/1.5 Torr). ^{1}H-NMR ($CDCl_3$): 7.53–7.58 (*m*, 1 arom. H); 7.12–7.25 (*m*, 3 arom. H); 5.33, 5.19 (H_{cis} and H_{trans} of CH_2=); 2.17 (*m*, $J(Me,H_{cis}) = 1.4$, $J(Me,H_{trans}) = 0.7$, Me); 4.20 (*s*, MeO). ^{13}C-NMR ($CDCl_3$): 156.9 (C(2)); 140.0 (C(3a)); 117.6 ($^1J = 162.3$, C(4)); 121.2 ($^1J = 160.8$, $^3J = 7.6$, C(5)); 121.8 ($^1J = 161.5$, C(6)); 109.4 ($^1J = 163.4$, C(7)); 133.6 (C(7a)); 137.7 (Me*C*=CH_2); 113.1 ($^1J = 159.8$, $^3J = 4.0$, MeC=C*H_2*); 20.7 ($^1J = 128.4$, $^3J = 8.9$, 4.3, *Me*C=CH_2); 57.2 ($^1J = 147.7$, MeO).

*3-[(1*H*)-Perimidin-2(3*H*)-ylidene]propan-2-one* (**21**). M.p. 241–245° ([38]: m.p. 258–260°). ^{1}H-NMR ((D_6)DMSO): 11.88 (*s*, 2 NH); 7.23 (*dd*, H–C(5), H–C(8)); 7.14 (*dd*, H–C(6), H–C(7)); 6.58 (*dd*, H–C(4), H–C(9)); 4.82 (*s*, C*H*COMe); 1.91 (*s*, Me); $J(4,5) = J(8,9) = 7.1$, $J(5,6) = J(7,8) = 8.3$, $J(4,6) = J(7,9) = 1.1$. ^{13}C-NMR ((D_6)DMSO): 191.0 (CO); 152.0 (C(2)); 134.2 (C(3a), C(9a), C(6a)); 128.3 ($^1J = 160.0$, C(5), C(8)); 118.7 ($^1J = 163.0$, $^3J = 6.9$, 4.1, C(6), C(7)); 115.8 (C(9b)); 105.1 ($^1J = 162.3$, $^3J = 7.5$, $^2J = 2.0$, C(4), C(9)); 80.2 ($^1J = 161.6$, *C*HCOMe); 28.5 ($^1J = 126.0$, Me).

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