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THE PHOTODIMERS OF α-PYRIDONES

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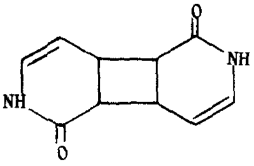
THE irradiation of α-pyridone has recently[1] been reported to give a dimer to which the structure (1) has been attributed. Related structures have been proposed[2] for dimers of uracil and thymine.



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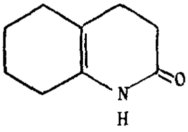

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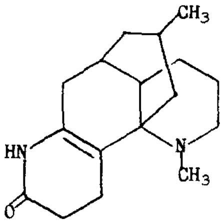

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The structure (1) contains the system $-\overset{|}{C}=\overset{|}{C}-\overset{|}{N}-\overset{|}{C}O$. This system is

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[1] E.C. Taylor and W.W. Paudler, Tetrahedron Letters No. 25, 1 (1960).

[2] S.Y. Wang, Nature, Lond. 190, 690 (1961).

present in 3,4,5,6,7,8-hexahydrocarbostyril[3] (2) and in α-obscurine[4] (3). These substances have absorptions with λ_{max} 253 (log ε 3.69) and λ_{max} 255 (log ε 3.73), respectively, in the ultraviolet. These observations are incompatible with the otherwise very reasonable structure proposed for α-pyridone dimer (1) since this, its N-methylated derivative and the other dimers described here have no such high intensity band in the ultra-violet. In the infra-red spectrum, furthermore, no band compatible with that to be expected from a vinyl lactam is to be found. These same facts also exclude from consideration the 1:2-1:4 Diels-Alder type adduct and strongly suggest that the dimer is formed by 1:4 addition of the dienic system to itself.

Experimental proof of the correctness of this was obtained in a simple manner. Irradiation of 4-methyl-N-methyl pyridone gave a dimer[*] [m.p. ca. 260° (dec.)]. If this were of the type (1) then the additional C-methyl substituent should be at a bridgehead. On the other hand if it were derived by 1:4 addition then it should be on a double bond. The NMR spectrum (doublet at 8.15τ) clearly indicates the latter to be correct. Furthermore, the ratio of vinyl to methine protons is now 1:2. The reverse argument obtains in the case of the dimer [m.p. 210-12° (dec.)] derived from the irradiation of 6-methyl-N-methyl pyridone. The position of the single band in the NMR (8.37τ), together with the fact that the ratio, vinyl:methine H is 2:1, indicates the quanternary nature of the methyl group. Since it has been shown[1] that N-methyl pyridone gives the same photodimer as obtained by the methylation of the pyridone dimer, and since it is well known[5] that alkylation of an ethylenic linkage is no impediment to the cyclobutane

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[*] Satisfactory analyses and molecular weights have been recorded.

[3] A.D. Campbell and I.D.R. Stevens, J.Chem.Soc. 959 (1956).

[4] W.A. Ayer and G.G. Iverach, Tetrahedron Letters No. 10, 19 (1960).

[5] e.g. E. Zavarin, J.Org.Chem. 23, 47 (1958).

type of dimerization, the general nature of the pyridone dimer must be considered as established. It has analogy in the dimerization of anthracene.[6]

Four structures for the parent N-methylated dimer (4, A-D, R = R' = H, R'' = Me) are then possible. A study of the NMR spectrum suggests that A is correct, and this structure is also compatible with dipole moment measurements.[1]

The 60 Mc/sec spectrum (5% in $CDCl_3$) shows three groups of peaks: (a) 14 lines between 363.5 and 407.4 cps from TMS (olefinic protons), (b) a 16 line pattern from 205.3 to 249.0 cps (methine H's), and (c) a strong singlet at 168.1 cps (7.20τ, $N\text{-}CH_3$). Both (a) and (b) have the appearance of AB systems in which both the A and B bands are split by two additional spin-spin couplings. For the methine pattern, the chemical shifts for A and B are 215.4 cps (6.41τ) and 238.3 cps (6.03τ), respectively with J_{AB} = 10.0 cps. The chemical shifts for the olefinic protons are 372.2 cps (3.80τ) and 398.6 cps, (3.36τ), J_{AB} = 8.2 cps. The rest of the coupling constants are listed in Table 1.

Table 1

Coupling Constant for the Photodimers

(±0.1 cps)

Dimer of	$J_{36'}$*	J_{34}	J_{35}	J_{45}	J_{46}	J_{56}	$J_{5\text{-}CH_3}$
N-Me pyridone	10.0	6.4	1.4	8.2	1.6	6.6	-
N-Ac pyridone	10.6	6.8	1.6	8.3	1.6	7.0	-
N-Me-4-Me pyridone	10.1	-	2.1	-	-	6.8	1.7

* Numbering as in 4A

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[6] D.E. Applequist et al., J.Am.Chem.Soc. 81, 457 (1959) and papers there cited.

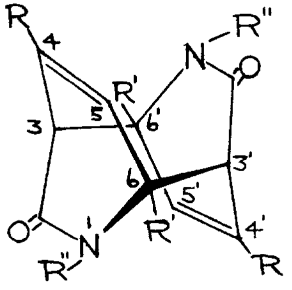
Using Dreiding models, it is apparent that in 4A (R = R' = H; R'' = Me) the olefinic protons (on C_5,C_5') lie approximately over the $>C = O$ grouping while the other two (on C_4,C_4') do not. This would lead to a difference in their respective chemical shifts. Furthermore, each of the methine protons is spin-spin coupled to three other nuclei. These two facts are compatible with the above observations and furnish support for the trans-anti formulation (A) over the other possibilities.

Apart from chemical shift differences, the N-$COCH_3$ (4, R = R' = H, R'' = Ac) dimer gives a similar spectrum (5% in $CDCl_3$). The methine protons appear at 4.64 and 6.19τ, while the olefinic H's are at 3.42 and 3.86τ. The coupling constants are listed in the table.

The spectrum (in $CDCl_3$) of the 4-methyl derivative 4 (R'' = R = Me, R' = H) is simplified. Since one of the olefinic protons has been replaced with methyl (doublet at 8.14τ, J = 1.7 cps), only 8 lines appear in the methine region. This pattern is, again, and AB system but each band is split by only one further interaction. The chemical shifts are A, 6.60τ, and B, 5.96τ and J_{AB} = 10.1, J_{AX} = 2.1 J_{BX} = 6.9 cps. The olefinic proton (3.75τ) appears as the expected multiplet for couplings of 6.9 and 2.1 cps with the methine protons and a weak coupling (J = 1.7 cps) with the neighbouring methyl group. It should be noted that the chemical shift of this proton corresponds closely to one of those in both the N-Me and the N-$COCH_3$ dimers. This proton (on C_5) is presumably slightly shielded by the neighboring C = O group. In this case, also, the dimer appears to be of the 4A type, which is compatible with dipole measurements (see below).

The NMR spectrum (in $CDCl_3$) of the 6, N-dimethyl derivative (4, R^1 = R^{11} = Me, R = H) is much simpler. In addition to singlets for N-CH_3 (7.20τ) and C-CH_3 (8.37τ), there are two lines in the olefinic region (396.0, 373.4

4A



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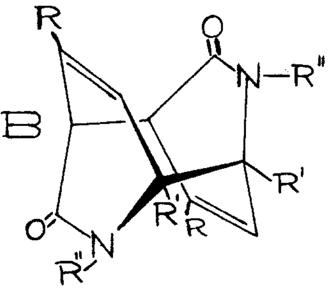
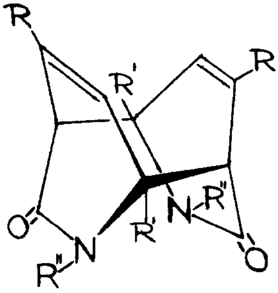
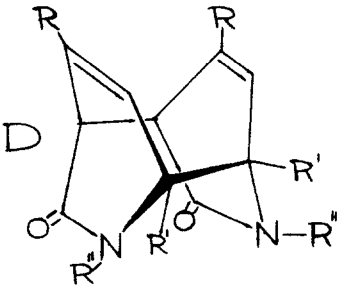


4C



4D



cps) and three in the methine region (189.5, 194.0, 198.5 cps). These results would suggest the exclusion of a structure of type 4A, since the olefinic protons are not greatly different.

Dipole measurements (in $CHCl_3$) indicate that the value for both the 4-methyl and the 6-methyl derivative is less than 2D.[7] Calculation indicates[7] that structures of type 4B and D should have dipoles greater than 4D. These results support the 4A type for the 4-methyl derivative, and, with the NMR evidence, suggest type 4C for the 6-methyl derivative.

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[7] We are greatly indebted to Professor N.L. Allinger (Wayne) for these determinations and the calculations. We understand Professor Allinger will be reporting the dipole data in detail elsewhere.

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