Mesoionic Six-Membered Heterocycles. XIV (1).
Crystal Structure of a Pyrimidine Betaine

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The crystal structure of a mesoionic pyrimidine was determined by means of an X-ray structure analysis.
The structure is discussed in terms of Dähne's concept as consisting of two coupled polymethines.

Introduction

Among the known mesoionic six-membered ring system (2), the pyrimidine derivatives have so far been most thoroughly studied due to their easy accessibility (3-6), their stability, their potential biological activity (5,6) and as educts for cycloadditions (5-7). Various graphical representations have been suggested for this class of compounds [A: Potts (4); **B**: Coburn and Glennon (5,6); **C**:Kappe (7)]. We prefer formula **C**, since we believe that it
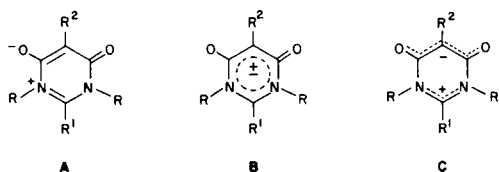
gives the most realistic indication for the charge distribution and for the actual distribution of bond orders.
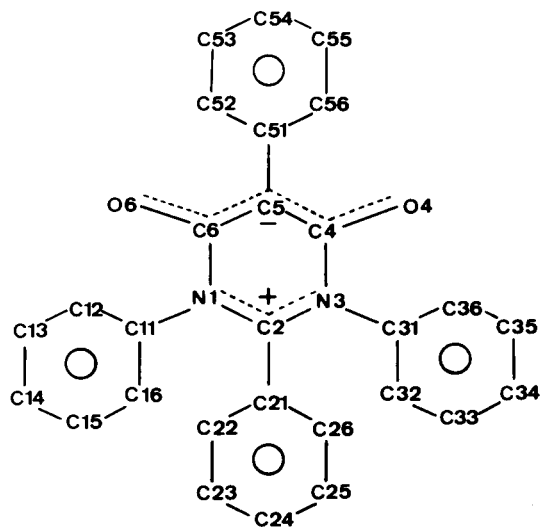

Figure 1. Atom numbering used for the crystal structure.

TABLE 1

FRACTIONAL ATOMIC COORDINATES OF THE ATOMS IN THE ASYMETRIC UNIT (X10000)
E.S.D.'S (IN PARENTHESIS) ARE IN UNITS OF THE LAST FIGURE

Atom	x	y	z
N1	2253 (11)	1908 (13)	1805 (14)
C2	2224 (13)	1458 (17)	1145 (19)
N3	1873 (11)	1641 (13)	471 (14)
C4	1521 (14)	2326 (17)	392 (20)
O4	1262 (11)	2434 (13)	-314 (15)
C5	1522 (13)	2770 (17)	1107 (16)
C6	1900 (13)	2600 (16)	1843 (18)
O6	1973 (10)	2939 (12)	2497 (13)
C11	2623 (14)	1728 (17)	2565 (17)
C12	3218 (14)	1883 (19)	2621 (19)
C13	3567 (14)	1677 (24)	3340 (22)
C14	3331 (19)	1338 (24)	3982 (21)
C15	2736 (20)	1206 (23)	3929 (21)
C16	2374 (14)	1393 (20)	3220 (21)
C21	2603 (15)	795 (16)	1133 (17)
C22	3158 (16)	856 (20)	839 (20)
C23	3520 (17)	232 (26)	838 (26)
C24	3330 (20)	-435 (24)	1131 (24)
C25	2781 (20)	-485 (19)	1409 (22)
C26	2419 (15)	114 (18)	1420 (21)
C31	1786 (14)	1131 (16)	-220 (18)
C32	2102 (15)	1224 (21)	-909 (21)
C33	1977 (16)	781 (26)	-1603 (23)
C34	1545 (17)	236 (21)	-1614 (20)
C35	1242 (15)	141 (18)	-930 (22)
C36	1361 (13)	585 (19)	-226 (18)
C51	1122 (13)	3423 (17)	1085 (18)
C52	1282 (16)	4056 (19)	1537 (22)
C53	890 (22)	4663 (20)	1524 (28)
C54	347 (22)	4636 (26)	1089 (30)
C55	196 (17)	4004 (27)	642 (26)
C56	565 (15)	3396 (21)	629 (21)
N1'	263 (11)	735 (14)	6924 (15)
C2'	0 (0)	1112 (27)	7500 (0)
C5'	0 (0)	-454 (25)	7500 (0)
C6'	331 (15)	-78 (19)	6931 (19)
O6'	639 (11)	-346 (13)	6431 (15)
C11'	534 (15)	1116 (17)	6252 (18)
C12'	1112 (16)	1357 (20)	6394 (21)
C13'	1369 (18)	1694 (23)	5725 (30)
C14'	1031 (23)	1795 (23)	4973 (29)
C15'	461 (21)	1550 (24)	4841 (22)
C16'	211 (15)	1206 (21)	5493 (21)
C21'	0 (0)	1920 (27)	7500 (0)
C22'	-343 (14)	2312 (20)	6880 (18)
C23'	-336 (14)	3088 (20)	6880 (19)
C24'	0 (0)	3456 (27)	7500 (0)
C51'	0 (0)	-1277 (28)	7500 (0)
C52'	-524 (14)	-1673 (20)	7391 (21)
C53'	-527 (16)	-2435 (22)	7391 (24)
C54'	0 (0)	-2827 (29)	7500 (0)

Pyrimidine mesoions could therefore be regarded as coupled polymethines [Dähne (8) - in the present case a combination of a monomethinecyanine with a trimethine oxonolate], similar to the class of 2, 5-diamino-1, 4-benzo-quinones, where the applicability of Dähne's concept was justified by several X-ray crystal structure analyses (9).

Upon heating, *N,N'*diphenylsubstituted pyrimidine betaines react to form 4-quinolones (10). The analogous reaction for the isoelectronic 1, 3-thiazines was discovered by Potts (11), who postulated the reaction to proceed via a

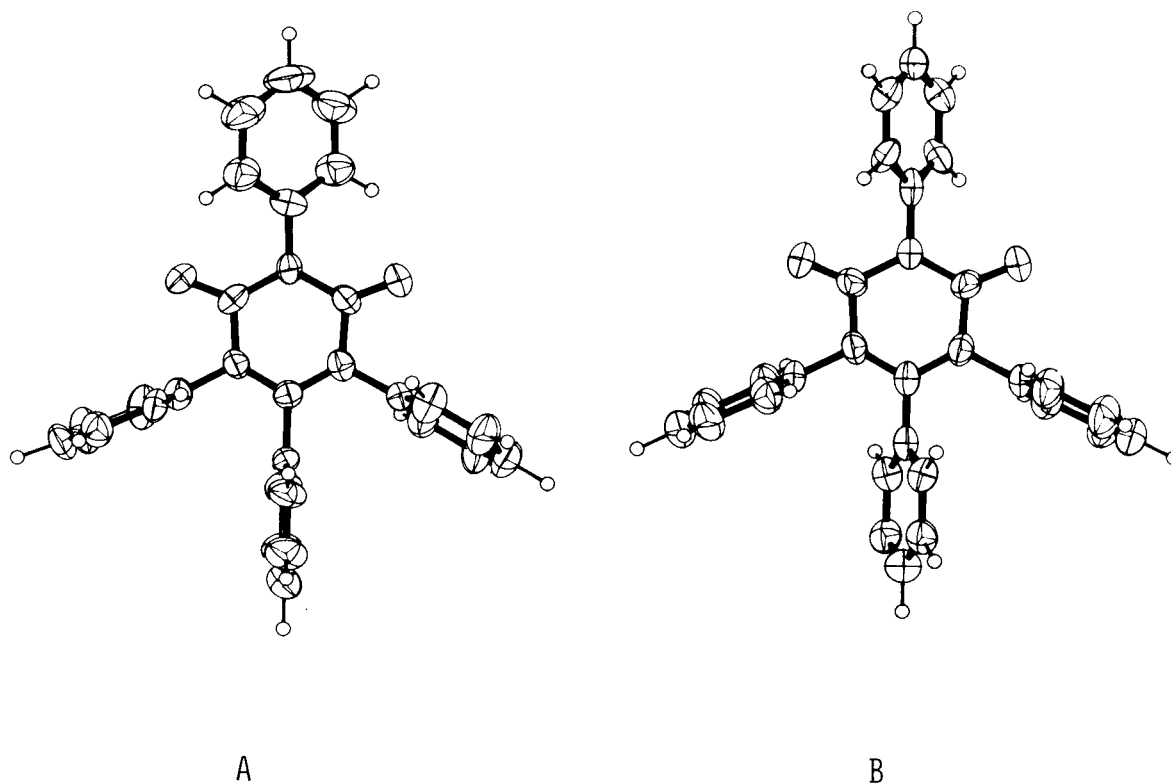A   B

Figure 2.   Projection of the two crystallographically independent molecules into the plane of the pyrimidine ring. A: molecule in the general position. B: molecule on the crystallographic twofold axis.
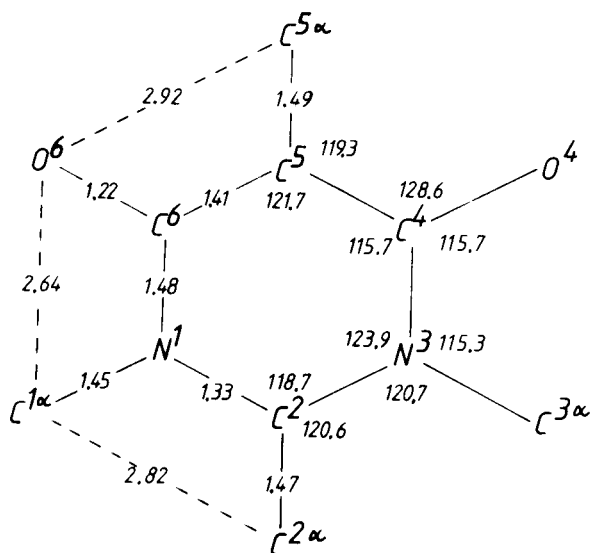

Figure 3: Averaged bond lengths and bond angles. Standard derivations of the averaged parameters: bond lengths, $\sigma \sim 0.01$ Å; bond angles, $\sigma \sim 1°$.
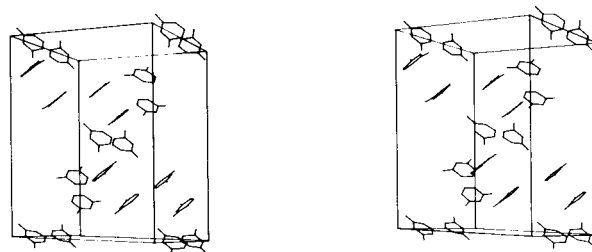

Figure 4. Packing diagram for the crystal structure of tetraphenylpyrimidine betaine. The phenyl groups have been omitted for clarity. The **a** axis runs horizontally across the page, the **b** axis runs vertical and the **c** axis runs roughly perpendicular to the plane of the paper.

showdeviations from planarity indicating some flexibility to facilitate formation of this bond. We report the crystal structure analysis of the tetraphenylpyrimidine betaine (R = R[1] = R[2] = phenyl), which was carried out to contribute to the above questions.

EXPERIMENTAL

X-Ray Structure Determination.

    Two crystal forms of the tetraphenyl pyrimidine betaine were obtained

bicyclic intermediate with a direct junction between C-2 and C-5. It might therefore be speculated that the mesoionic pyrimidine betaines are not planar, but

from the same mother liquor: long, triclinic needles (approximate cell dimensions from precession photographs: a = 9.82, b = 11.48, c = 11.54 Å, α = 105.53, β = 104.82, γ = 113.18°), and smaller prisms of rhombohedral shape. The structure determination was carried out from the latter crystal form, using a specimen of approximate dimensions 0.1 × 0.12 × 0.25 mm.

Space group and approximate cell dimensions were determined by least-squares refinement of the setting angles of 11 reflections, on a Stoe 4-circle diffractometer with graphite-monochromated MoK$_\alpha$-radiation (λ = 0.71069 Å): $C_{28}H_{20}N_2O_2$, monoclinic, C2/c, a = 22.719 (2), b = 18.025 (3), c = 16.046 (2) Å, β = 95.77 (1)°, Z = 12, d_x = 1.27 g cm^{-3}.

All 4009 independent reflections with 2θ < 44° ($\sin\theta/\lambda$ < .53) were subsequently measured in the $\omega/2\theta$-scan mode (ω scan width: .5°). The data were processed to yield 1350 reflections with I > 2.5 σ (I) (I = a (s-kb); σ(I) = a (s + k²b + c)$^{1/2}$; F = (lI)$^{1/2}$; σ(F) = (F² + 1σ (I))$^{1/2}$ – F; a = scale factor to correct for drift in standard intensities, s = total count from intensity scan, b = total count from background measurements, c = factor determined from observed standard intensity fluctuations (12), l = LP-factor). No absorption correction was applied (μ(MoK$_\alpha$) = 0.87 cm^{-1}). The structure was solved with direct methods and refined with full matrix and block-diagonal matrix techniques. In the terminal refinement stages, hydrogen atoms were included in the structure factor calculation at calculated positions, but not refined. With anisotropic temperature factors for all non-hydrogen atoms, the refinement converged at a residual of R = 0.053 (1/σ^2 (F) weights) (12).

Discussion

Atomic coordinates for the asymmetric unit are given in Table 1. Since there are 12 molecules in the unit cell, there must be two kinds of molecules in this crystal structure: molecules A, which lie on a general position (Z = 8), and molecules B, situated on a crystallographic twofold axis passing through the atoms C2, C5, C21, C24, C51 and C54 (Z = 4). Figure 2 shows an ortep-drawing of the two crystallographically unrelated molecules, projected into the plane of the pyrimidine ring. It is apparent that the two kinds of molecules differ significantly as far as the twist of the phenyl groups with respect to the pyrimidine ring is concerned. The distribution of bond length and bond angles, however, agrees within the respective standard deviations (bond lengths: .02 – .04 Å; bond angles: 2-4°) between the two kinds of molecules and, in fact, between the two crystallographically unrelated halves of molecule A. We have therefore averaged bond lengths and bond angles for the three independent molecule halves (Figure 4).

The molecular geometry is in convincing agreement with the mesoionic formula C. The N (1) -C (6) bondlength of 1.48 Å is as long as a sp³ – sp³ single bond and exceeds the bondlength expected for an amide bond by 0.15 Å. The observed value is quite consistent with the corresponding bondlengths in the 2, 5-diamino-1, 4-benzoquinone (9) and much longer than the N-C distances observed in the crystal structures of the barbiturate anion (13) (1.39 Å) and some of its derivatives (14) (1.34 -1.40 Å). We therefore believe that Dähne's concept is an adequate description for mesoionic 6-ring compounds.

The deviations of the atoms of the pyrimidine ring from

a least-squares plane do not exceed 0.04 Å for either of the two molecules and are therefore trivial. Some flexibility of the molecule is, however, expressed by the fact that some of the α-substituent atoms deviate by as much as 0.2 Å from a least-squares plane through the pyrimidine ring; this is illustrated by the corresponding dihedral angles: C11-N1-C2-C21: -5°; C21-C2-N3-C31: 11°; C31-N3-C4-O4: -11°; O4-C4-C5-C51: 7°; C51-C5-C6-O6: -3°; O6-C6-N1-C11: 2°; C51'-C5'-C6'-O6': -2°; O6'-C6'-N1'-C11': 6°; C11'-N1'-C2'-C21': -3°.

Figure 4 shows a stereo-picture of a whole unit cell. It is apparent, that the molecules are packed in such a way, that dipole moments of adjacent molecules are roughly antiparallel.

Acknowledgment.

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